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MODULE IMPROVEMENT PROGRAM

FINAL REPORT

U.S. NAVY

BUREAU OF SHIPS
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AUGUST 31, 1962

CONTRACT NObs-84329
G.O. 80025-CE

Westinghouse Electric Corporation
CENTRAL RESEARCH LABORATORIES-PITTSBURGH 35, PA.

CONTENTS

I. SUMMARY

This final report on the Module Improvement Program, NObs 84329, presents additional data primarily related to the continued testing of materials for use in power generator modules. For more detail on the development and properties of these materials, reference is made to the Progress Reports, Nos. 1, 2, and 3 of this contract, and to the Progress Reports for NObs 86595 and 84317.

The objective of the program has been to improve the life-performance of thermoelectric generator modules by means of engineering development and evaluation in the areas of insulation, material processing, and contacting. During the program, it became apparent that the life-performance of materials would be strongly influenced by the stresses imposed by operating conditions, and that life-performance would be directly dependent on the mechanical properties of the thermoelectric materials and contacts. Therefore the program was modified to include a stress analysis and the testing of mechanical properties of materials.

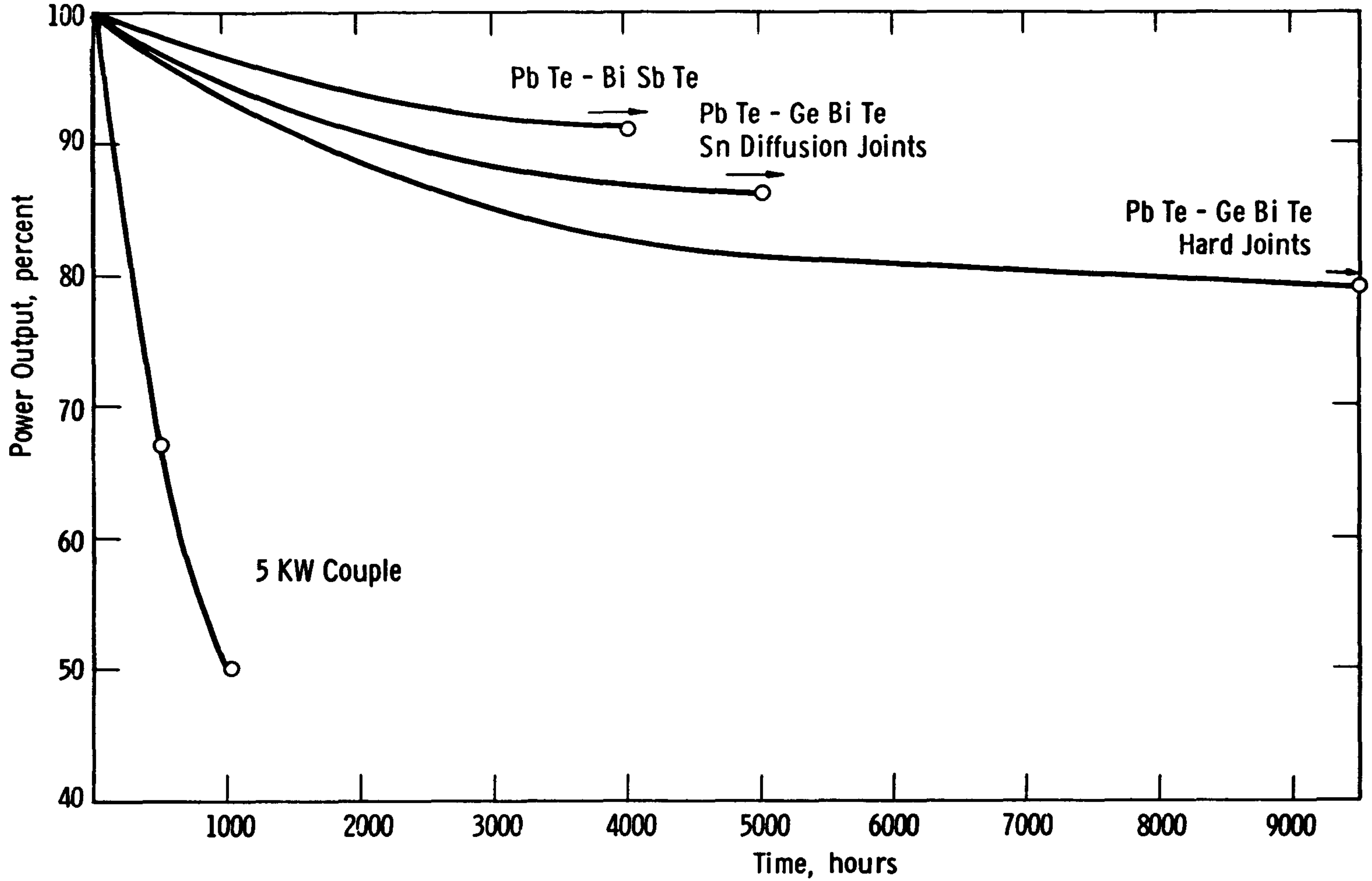
At the beginning of the program, state-of-the-art in generator module life-performance was represented by the couple technology of the 5 KW generator. Average life at that time was 400 hours for 25 percent drop in power output, and initial couple efficiency of 5 percent.

At the conclusion of the program, average module life is 7500 hours for 25 percent power drop, with some module tests running in excess of 10,000 hours. Module efficiency has been improved to 7 percent for a smaller temperature

gradient, which insures longer life. In Figure 1, where this relationship is shown graphically, it will be seen that several intermediate points are plotted for more recent developments. The behavior of these is such as to indicate that life-performance will be at least equivalent to the 10,000 hour tests now completed.

Three module sections, with a combined power output slightly above 30 watts, have been assembled using the material-couple systems for which performance data are shown in Figure 1. The module sections were operated for 100 hours in our laboratory, and were then delivered to the Engineering Experiment Station at Annapolis, Maryland, where they will be put on extended life-performance test.

With the demonstration of life approaching one year of operation at useful power levels, it may be concluded that thermoelectric power generation is very close to practical application for remote and portable power packs. Additional development is needed to improve the consistency and reliability of the couples. This work falls generally into two areas: the completion of the processing development, property measurement, and contacting evaluation for the presently used materials; and the continued development and module "proof tests" of several newer materials.


Pb Te - Bi Sb Te
Pb Te - Ge Bi Te
Sn Diffusion Joints
Pb Te - Ge Bi Te
Hard Joints
5 KW Couple
Power Output, percent
100
90
80
70
60
50
40
1000
2000
3000
4000
5000
6000
7000
8000
9000
Time, hours

II. INSULATING CORE COATINGS

At the beginning of the program, state-of-the-art was reviewed to establish criteria for insulating core coatings for use in thermoelectric power generation.

1. Operational capability in the temperature range 300°C-600°C.
2. Reliable service life of at least 10,000 hours.
3. Impervious to corrosion by thermoelectric materials.
4. Absence of porosity.
5. Resistance to thermal shock and cycling.
6. Stability under reducing atmosphere.
7. Low thermal drop.
8. High resistivity (10^6 ohm-cm) and dielectric strength (min. 40 V/mil)
9. Ease of application.
10. Good bearing strength.

High temperature stability, electrical properties, and thermal conductivity of filled and unfilled organic resins, glasses, inorganic sheet insulation and plasma sprayed inorganic oxides were measured. Evaluation of results narrowed the materials searching to inorganic oxides, both in sheet form, and in the form of plasma sprayed films. It became apparent that the source of major temperature drop was the interface rather than the material itself. Therefore, emphasis was changed to explore

methods for minimizing the interface temperature drop of the inorganic oxides. Plasma jet coating of the oxide on the metal core was investigated as a means of "fusing" the coating to get low temperature drop across one interface. Methods were developed for plasma jet spraying that would apply a coating of uniform, high dielectric strength. To minimize the other interface temperature drop, liquid metals were investigated. These, of course, must be non-reactive with the core coating at elevated temperature.

Samples of several core coatings with and without liquid metal interfaces were prepared and put on life test. The following Memo summarizes the results:

Research Labs. Memo No. M-62136-6
Insulation & Chemistry Tech. Dept.

July 18, 1962

TERMINATION OF AGING OF INORGANIC OXIDE COATINGS IN PRESENCE OF THERMOELECTRIC ELEMENTS

D. W. Lewis

As described in Materials Research Laboratories Report No. 62147-24405*, the change in temperature drop and resistivity of several plasma sprayed alumina and magnesia coatings, and one of evaporated silicon monoxide, were measured as these coatings were aged in the presence of T/E elements. At the same time, the effectiveness of gallium-indium liquid alloy in reducing the thermal resistance of the hot strap-core coating interface was also determined. During aging, 160 volts D. C. was applied across the coating. A pressure of 30 psi was applied at the contact of the hot strap with the core coating. The units were cycled four times a day between aging temperature and tap water temperature (about 20°C). Shutdown periods were 2 hours long so that heat and voltage were on only 16 out of 24 hours. In all tests, the cold core was in contact with a water-cooled heat sink.

Aging of the first three coatings in the table was at 325°C, but after 2600 hours, the temperature was raised to 350°C. BiTe pellets were

*<u>Module Improvement Program</u>, Progress Report No. 3, March 15, 1962

present in all three units. The heat flux through each of these three coatings was 32.5 watts/in.^{2}. Just before termination of the tests after 7800 hours at 350°C, the resistivity of all three were in the range of 10^{10} to 10^{11} ohm-cm. at temperature. The temperature-measuring thermocouple attached to the magnesia coating was broken during aging, but earlier temperature drops were similar to the alumina coating. Wetting of the interface between the 1.1 mil alumina surface and the T/E strap lowered the temperature drop to 6.5 to 8 °C. The coatings were in excellent condition at the end of the tests. Gallium-indium was still a bright liquid metal. Incidentally, a similar test at 515°C showed that Ga-In is effective for only a few hundred hours. At this temperature, it reacts with oxygen and metallic straps.

A 3 mil plasma sprayed magnesia coating was aged for 3565 hours at 500°C in the presence of GeBiTe pellets. The temperature drop varied during this time from 18 to 28°C and the resistivity from 10^{10} to 10^8 ohm-cm. The thermal flux through the system was 68 watts/in.^{2} as determined by a calorimetric measurement of the heat output. Some chipping of the coating from the hot core was beginning to occur.

A 2.3 mil coating applied by evaporation of silicon monoxide was aged for 1700 hours at 500°C in the presence of GeBiTe pellets. During this time, the temperature drop increased from 26° to 45° with a heat flux of 70 watts/in.^{2}. At the beginning, the resistivity was 10^{10} ohm-cm. When a short occurred after 1700 hours, the test was stopped. The coating was severely cracked.

Plasma sprayed alumina coatings, 3.5 mils thick, were aged at 510°C in two assemblies in the presence of 8 SNAP-10 couples. In one, the coating was applied to the hot core on which the couples were pressed. In the other, the coating was applied to the hot straps of the 8 couples. The temperature drop at the various couples varied roughly from 28 to 53°C, resulting from slight irregularities in the height of the couples. However, the temperature drop at any one couple remained quite constant over the full aging period. The heat flux through both of these systems was 38 watts/in.^{2}. The resistivity of the coating on the hot core remained at 10^{10} to 10^{11} ohm-cm. throughout, while a short occurred after 4500 hours at 510°C in the assembly which had the alumina on the couple straps. From the appearance of the coatings, the exact opposite would be expected. The coating was cracking away from the core and when the couples were lifted off the coated core, some of the coating remained stuck to the couple strap. The coatings applied to the individual couple straps were still intact.

It would appear from these results that plasma sprayed alumina or magnesia would function as T/E core coatings indefinitely at 350°C in the presence of BiTe elements. Also, gallium-indium liquid alloy is effective in reducing the interfacial thermal drop in this environment. These coatings would te effective for shorter periods at 510°C under the severe thermal cycling prevailing in these tests.

RESISTIVITY AND TEMPERATURE DROP ACROSS INORGANIC OXIDE COATINGS AGED IN PRESENCE OF THERMOELECTRIC ELEMENTS

Coating	Core Material	Thickness (Mils)	Hours/°C	Pressure (psi)	Heat Flux (Watts/in2)	Temp. Drop (°C)	Resistivity(1) (ohm-cm)
M_gO	Al	1.0	2600/325	30	32.5	*	10^{11}
Al_2O_3+GaIn	Al	1.1	Plus	30	32.5	6.5-8	10^{11}
Al_2O_3	Al	1.3	7800/350	30	32.5	10-11	10^{11}
M_gO	Stainless Steel	3.0	3565/500	30	91	18-28	10^{10}-10^{8}
SiO	Stainless Steel	2.3	1700/500	30	94	26-45	10^{11}-10^{9} Sudden short at 1700 Hrs.
Al_2O_3	Stainless Steel	3.5	6285/510	30	38	28-53**	10^{11}-10^{10}
Al_2O_3 on straps of SNAP-10 couples		3.5	5712/510	30	38	29-45**	10^{11}-10^{10} Sudden short at 4500 Hrs.

(1) Resistivity measured at temperature.

*Temperature-measuring thermocouple broken.

**Range of measurements at straps of 4 of 8 SNAP-10 couples.

III. MECHANICAL PROPERTIES

Mechanical properties of various compositions of ZnSb, PbTe, and GeBiTe have been reported.* In the following section, additional mechanical properties are reported for another material (BiSbTe) and for GeBiTe having two different sintering treatments.

Mechanical Properties of Pressed BiSbTe in Compression Perpendicular to Pressing:

Three heats of BiSbTe were tested in compression from room temperature to 450°C. One heat had a 1% addition of gold, the second 5% gold, and the third no gold. The ultimate strength, Young's modulus of elasticity, and Poisson's ration were measured. None of the specimens tested exhibited a 0.2% yield strength; failure was always reached before the 0.2% yield.

At room temperature, SR-4 resistance strain gages were used to measure the strain, and at elevated temperatures a 2" SR-4 extensometer was used. Two specimen sizes were tested. All specimens 1/4" wide by 1/4" thick were 1" long, and specimens 3/8" wide by 1/4" thick were 1/2" long. With both specimen sizes, the load was applied in the length direction, which is perpendicular to pressing. The extensometer was used with the 1" specimens only. It was fixed to two platens 1/2" in diameter at each end of the specimen. As the specimen compressed, the platens followed the deformation which was measured by the extensometer. The platens

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*Module Improvement Program, Progress Report No. 3, March 15, 1962

were hardened and the compressive loads low so that a negligible deformation occurred in the platens.

The results are tabulated in Table 1 and presented graphically in Figure 1. They indicate that the gold additions did not significantly affect the mechanical properties of BiSbTe. More tests are needed for conclusive proof.

TABLE 1

MECHANICAL PROPERTIES OF PRESSED BiSbTe
IN COMPRESSION PERPENDICULAR TO PRESSING

Specimen Mark	Width Inches	Thickness Inches	Test Temp. °C	Ultimate Stress Lbs.	Ultimate Stress Psi	Modulus of Elasticity Psi	Poisson's Ratio
3276-1	0.376	0.247	RT	1205	12950	3.5×10^6	0.17
-2	0.249	0.250	RT	583	9350	4.6 " "	0.25
-3	0.250	0.250	RT	592	9450	4.6 " "	0.20
-4	0.250	0.250	350	563	9000	3.4 " "	+
-5	0.250	0.250	350	548	8750	3.1 " "	+
-6	0.376	0.247	400	262	2800	+	+
3341-1	0.250	0.249	RT	658	10550	5.3 " "	0.16
-2	0.376	0.250	RT	1085	11550	3.8 " "	0.22
-3	0.376	0.250	400	280	3000	+	+
-4	0.250	0.249	450	141	2250	+	+
3344-1	0.387	0.268	RT	920	9100	2.7 " "	0.20
-2	0.250	0.250	RT	625	10000	4.6 " "	0.29
-3	0.250	0.252	RT	678	10750	4.8 " "	+
-4	0.250	0.250	350	373	5950	2.2 " "	+
-5	0.250	0.250	350	652	10450	2.4 " "	+
-6	0.378	0.268	400	293	2900	+	+

+This property was not measured

NOTE: 1. None of the specimens exhibited 0.2% yield.

2. Heat #3276 = $Bi_{.5}Sb_{1.5}Te_3$ + 5% Au

3. Heat #3341 = $Bi_{.3}Sb_{1.7}Te_3$

4. Heat #3344 = $Bi_{.3}Sb_{1.7}Te_3$ + 1% Au

5. The data in this table is presented graphically in Figure 1.

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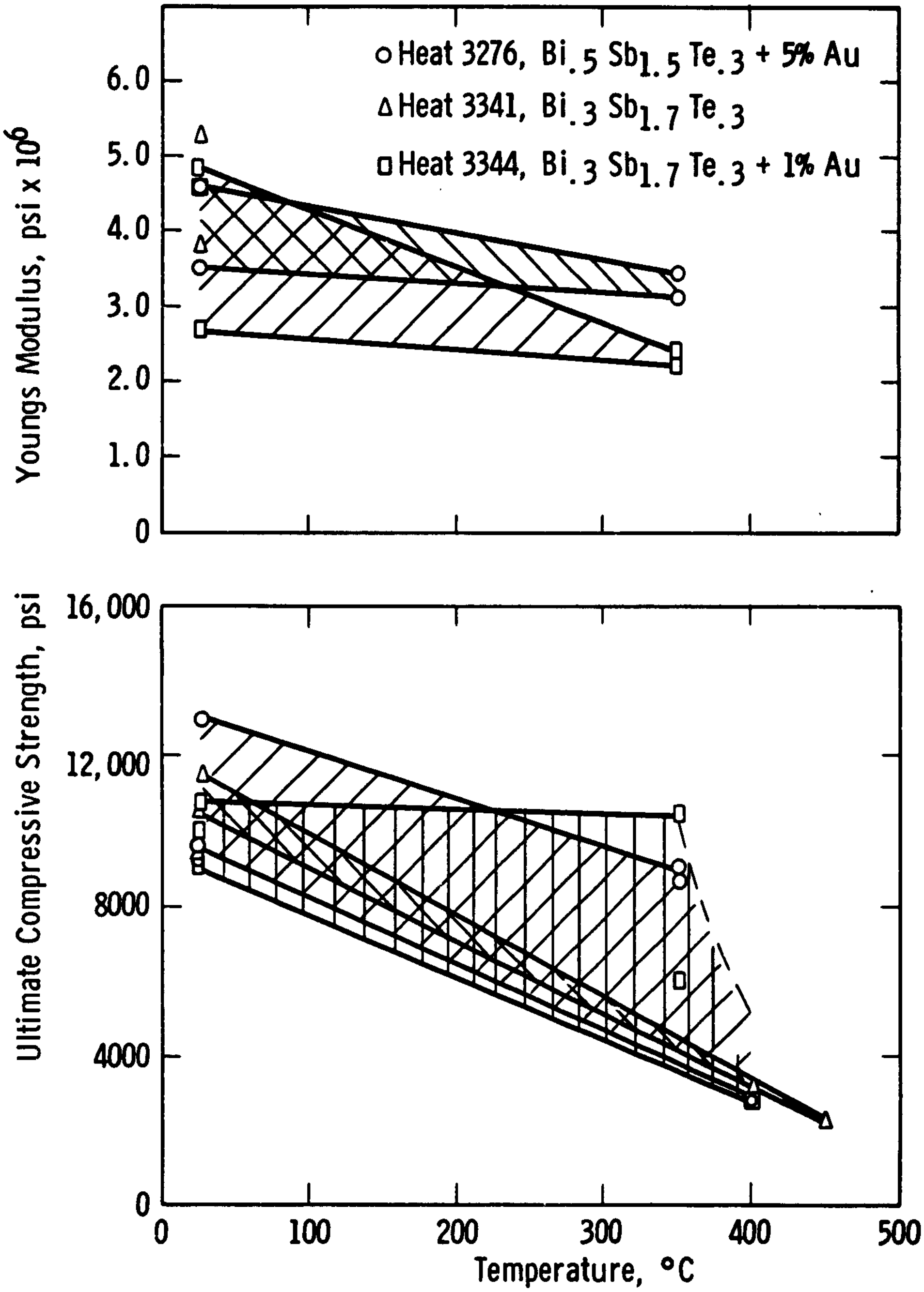

Fig. 1—Mechanical properties of pressed Bi-Sb-Te perpendicular to pressing direction

The Effect of Sintering Treatments and Composition on the Mechanical Properties of GeBiTe:

The effect of sintering treatment and composition on the mechanical properties of GeBiTe was determined. The mechanical properties were measured in compression at room temperature and 450°C, and the ultimate shear strength was measured at room temperature.

The room temperature compression and shear tests were conducted on pellets 1/2" diameter by 1/2" long. For the compression tests the load was applied parallel to the pressing direction, and in the shear tests the load was applied perpendicular to pressing. For the elevated temperature tests, three 1/2" diameter by 1/2" long pellets were stacked for each test. SR-4 resistance strain gages were used to measure the strain in the specimen at room temperature, and a one-inch SR-4 extensometer was used at the elevated temperatures to measure the strain over the central one-inch of the stack. The room temperature tests were conducted in an air atmosphere, while the elevated temperature tests were conducted in a flooded argon gas atmosphere. A detailed description of the testing procedure is given in Central Technical Services Report No. 62-173-567-R4*.

The composition of Heat Nos. 3365, 3366, and 3417 was $Ge_{0.93}Bi_{0.07}Te$ and the composition of Heat No. 3418 was $Ge_{0.95}Bi_{0.05}Te$. Two sintering treatments were used with Heat Nos. 3365, 3366, and 3417. Those marked dash H (-H) or dash one (-1) were sintered in hydrogen gas for 1-1/2 hours at 600°C plus 1/2 hour at 685°C. Those marked dash L (-L) or dash two (-2) were sintered in

*Module Improvement Program, Progress Report No. 3, March 15, 1962

hydrogen gas for 1-1/2 hours at 600°C and 1/2 hour at 665°C. Heat No. 3418-1 was sintered in hydrogen gas 1-1/2 hours at 600°C plus 1/2 hour at 685°C, and Heat No. 3418-2 was sintered in hydrogen gas for 3 hours at 600°C.

The compression test results are tabulated in Table 1 and Table 2 and the shear test data in Table 3. The compression test data is also presented graphically in Figures 1 to 4. Since the shear tests were conducted at room temperature only, the shear data is not presented graphically.

The data shows that the modulus of elasticity is higher for the heats with the higher sintering temperatures. These heats are marked -1 or -H. The ultimate compressive strength is also higher for these heats at room temperature. The ultimate compressive strengths of heats 3417 and 3418 at 450°C were about the same for both sintering treatments of each heat. With a few exceptions, none of the heats exhibited a 0.2% yield strength at room temperature. All heats exhibited a 0.2% yield at 450°C.

Some values of Poisson's ratio are low, and in general, the specimen with the low Poisson's ratio gave a low value for Young's modulus of elasticity. The low value of Poisson's ration could be the result of low density or microscopic cracks in the specimens.

TABLE 1

MECHANICAL PROPERTIES OF PRESSED GeBiTe IN COMPRESSION PARALLEL TO PRESSING
HEAT NOS. 3365-L, 3365-H, 3366-L, 3366-H

Specimen Identification		Diameter	Test Temp.	0.2% Offset Yield Stress Lbs.	0.2% Offset Yield Stress Psi	Ultimate Stress Lbs.	Ultimate Stress Psi	Modulus of Elasticity Psi	Poisson's Ratio
#3365-L	-1	.501	450 °C	520	2650	740	3750	1.2 x 10^6	++
	-2	"	"	391	2000	705	3600	0.7 "	++
	-3	"	"	481	2450	1415	7200	0.9 "	++
#3365-H	-1	"	"	1480	7500	1705	8650	2.7 "	++
	-2	"	"	1505	7650	1810	9200	3.4 "	++
	-3		"	+	+	310	1550	1.4 "	++
#3366-L	-1	"	"	513	2600	1430	7250	0.8 "	++
	-2	"	"	385	1950	1300	6600	0.9 "	++
	-3	"	"	856	4350	1670	8450	3.2 "	++
#3366-H	-1	"	"	1220	6200	1705	8650	1.5 "	++
	-2	"	"	1405	7150	1730	8800	1.7 "	++
#3366-L	-1	"	R.T.	+	+	1475	7500	1.8 "	0.09
	-2	"	"	499	2550	525	2650	1.3 "	0.03
	-3	"	"	+	+	1780	9050	1.6 "	0.06
#3366-H	-1	"	"	+	+	3595	18250	3.0 "	0.08
	-2	"	"	+	+	3220	16350	3.3 "	0.12
	-3	"	"	+	+	3300	16750	1.1 "	0.03
#3365-L	-1	"	"	998	5050	1242	6300	1.3 "	0.08
	-2	"	"	+	+	1280	6500	1.4 "	0.10
	-3	"	"	1000	5050	1183	6000	1.1 "	0.09
#3365-H	-1	"	"	+	+	2970	15050	4.9 "	0.23
	-2	"	"	+	+	2450	12450	2.4	0.09
	-3	"	"	+	+	2775	14100	0.6 "	0.16

+Specimen did not exhibit this property.

++This property was not measured.

NOTE: The data in this table is presented graphically in Figures 1 and 2.

TABLE 2

MECHANICAL PROPERTIES OF PRESSED GeBiTe IN COMPRESSION PARALLEL TO PRESSING
HEAT NOS. 3417-1, 3417-2, 3418-1, 3418-2

Specimen Identification		Diameter	Test Temp.	0.2% Offset Yield Stress Lbs.	0.2% Offset Yield Stress Psi	Ultimate Stress Lbs.	Ultimate Stress Psi	Modulus of Elasticity Psi	Poisson's Ratio
3417-1	-1	.502	R.T.	+	+	3490	17650	3.6×10^6	.13
	-2	"	"	+	+	2975	15050	6.6 "	.07
3417-2	-1	"	"	+	+	1513	7650	2.8 "	.04
	-2	"	"	+	+	1588	8000	3.0 "	.07
	-3	"	"	+	+	1390	7000	3.0 "	.04
3418-1	-1	.501	"	+	+	1438	7300	4.2 "	.12
	-2	"	"	+	+	1750	8900	3.6 "	.06
	-3	"	"	+	+	1505	7650	4.0 "	.07
3418-2	-1	.502	"	+	+	1013	5100	1.8 "	.04
	-2	"	"	+	+	1178	5950	3.0 "	.09
	-3	"	"	+	+	1195	6050	2.2 "	.09
3417-1	-1	.499	450°C	1863	9500	1875	9550	3.3 "	++
	-2	.498	"	1563	8000	1650	8450	2.4 "	++
	-3	.499	"	+	+	2090	10650	4.7 "	++
3417-2	-1	.502	"	1208	6100	1720	8700	1.7 "	++
	-2	.501	"	1105	5600	1940	9850	1.4 "	++
	-3	.502	"	1178	5950	2050	10350	2.3 "	++
3418-1	-1	.501	"	1213	6150	1850	9400	2.4 "	++
	-2	"	"	803	4050	1630	8250	2.3 "	++
3418-2	-1	.502	"	990	5000	1580	8000	1.1 "	++
	-2	.503	"	1075	5400	1460	7350	2.3 "	++
	-3	.502	"	1000	5050	1875	9450	1.4 "	++

+Specimen did not exhibit this property.

++This property was not measured.

NOTE: The data in this table is presented graphically in Figures 3 and 4.

TABLE 3

SHEAR STRENGTH OF PRESSED GeBiTe AT ROOM TEMPERATURE
MEASURED PERPENDICULAR TO PRESSING
HEAT NOS. 3365-L, 3365-H, 3366-L, 3366-H
3417-1, 3417-2, 3418-1, 3418-2

Specimen Identification		Diameter	Test Temp.	Ultimate Shear Stress Lbs.	Psi
3365-L	-1	.502	R. T.	240	1200
	-2	"	"	185	950
	-3	"	"	184	950
3365-H	-1	.495	"	204	1050
	-2	.494	"	305	1600
	-3	.501	"	397	2000
3366-L	-1	"	"	231	1150
	-2	"	"	203	1050
	-3	"	"	246	1250
3366-H	-1	.499	"	305	1550
	-2	.493	"	350	1850
	-3	.499	"	369	1900
3418-1	-1	.496	"	299	1550
	-2	.496	"	236	1200
	-3	.496	"	265	1350
3418-2	-1	.496	"	199	1050
	-2	.496	"	253	1300
	-3	.496	"	202	1050
3417-1	-1	.501	"	540	2750
	-2	.501	"	406	2050
	-3	.496	"	450	2350
3417-2	-1	.502	"	183	900
	-2	.502	"	204	1050
	-3	.502	"	161	800

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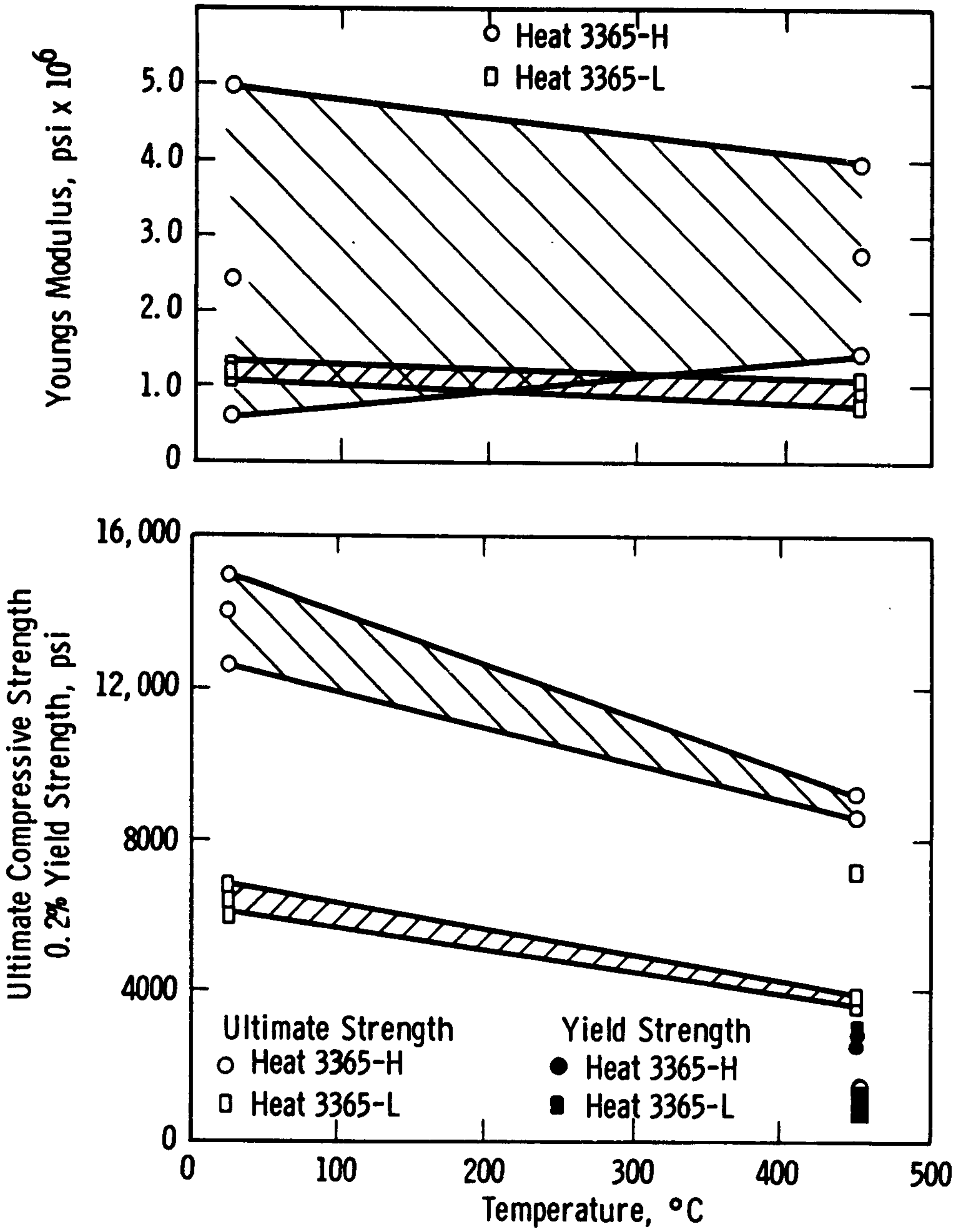


Fig. 1—Compressive strength of $Ge_{0.93}Bi_{0.07}Te$
Parallel to Pressing
Sinter: -H 600°C, 1½ Hours, H_2 + 685°C, ½ Hour, H_2
-L 600°C, 1½ Hours, H_2 + 665°C, ½ Hour, H_2

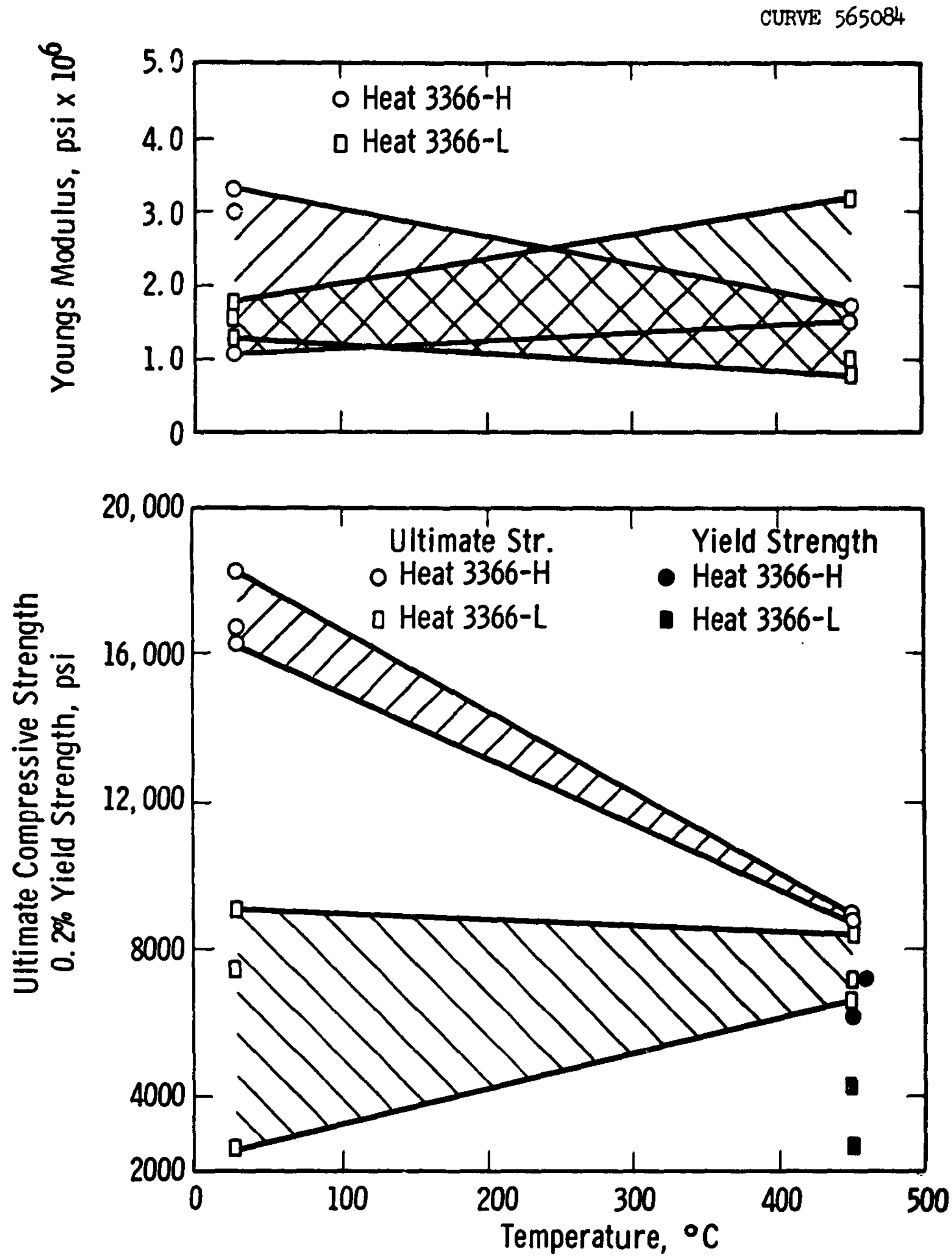


Fig. 2—Compressive strength of $Ge_{.93}Bi_{.07}Te$

Parallel to Pressing

Sinter: -H 600°C, 1½ Hour, H_2 + 685°C, ½ Hour, H_2

-L 600°C, 1½ Hour, H_2 + 665°C, ½ Hour, H_2

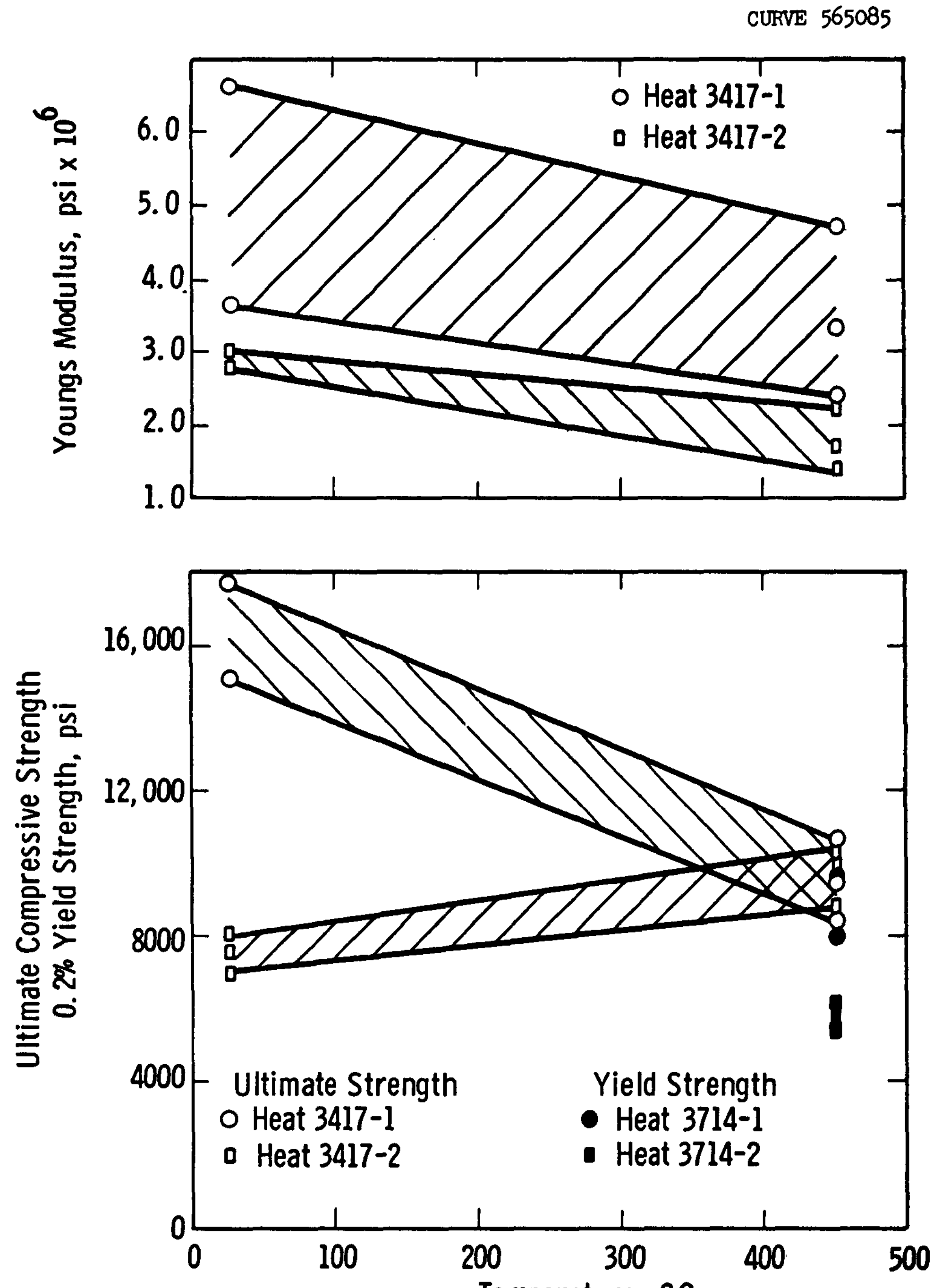


Fig. 3—Compressive strength of $Ge_{0.93}Bi_{0.07}Te$

Parallel to Pressing

Sinter: -1 600°C, 1½ Hours, H_2 + 685°C, ½ Hour, H_2

-2 600°C, 1½ Hours, H_2 + 665°C, ½ Hour, H_2

CURVE 565086

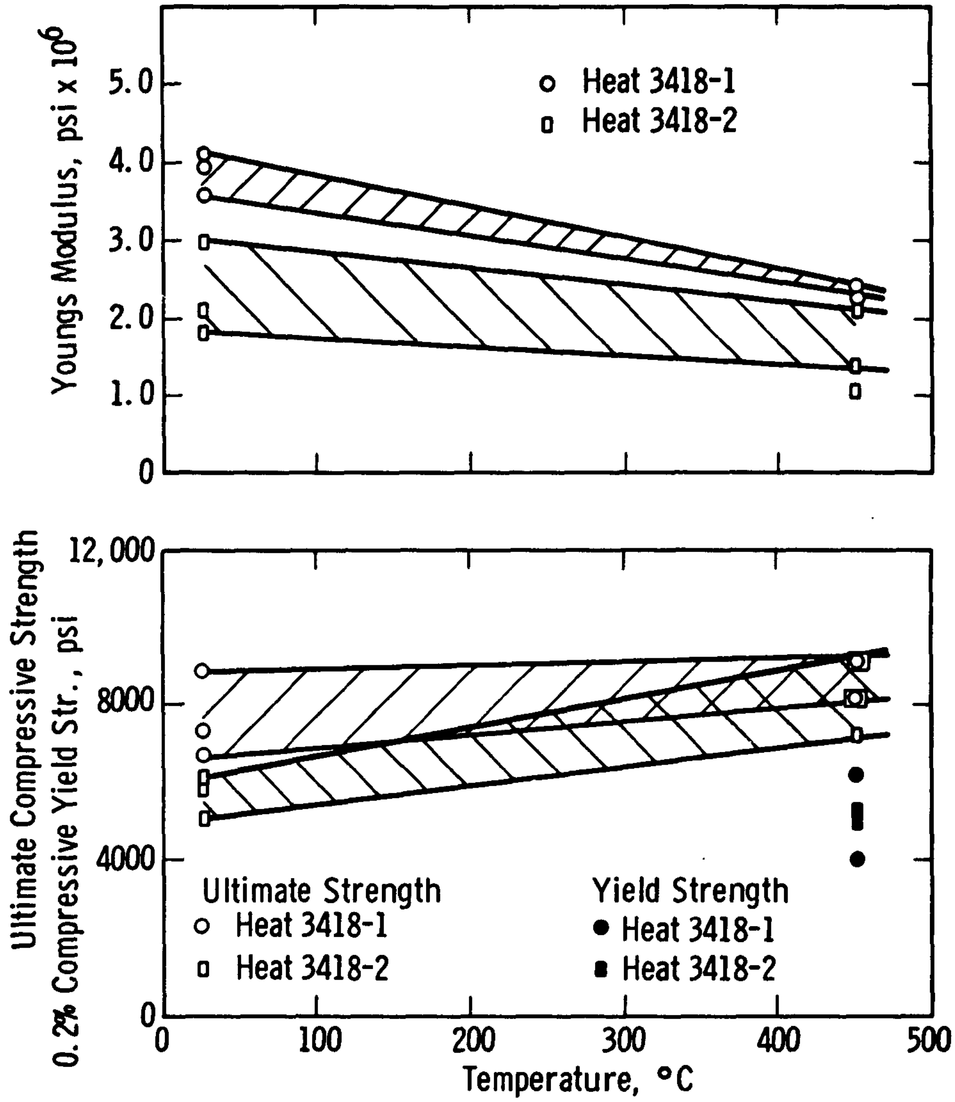


Fig. 4—Properties of $Ge_{0.95}Bi_{0.05}Te$ in compression Parallel to Pressing

Sinter: -1 600°C, 1½ Hours, H_2 + 685°C, ½ Hour, H_2

-2 600°C, 3 Hours, H_2

IV. TEST PROGRAM

Introduction:

The purpose of this extensive test program is to evaluate the performance of thermoelectric couples as to their life, power output, efficiency, mechanical and metallurgical construction and many other factors which might contribute to the successful operation of a static power conversion unit.

When a thermoelectric couple is assembled it forms a power producing system, which consists of thermoelectric elements, hot strap, spring braid assemblies and various contacting materials. This system when tested will give different performance results than will be obtained when the elements are tested separately. A further change of behavior is observed when a number of thermoelectric couples are integrated to form either a module or a full size generator. These changes are direct results of heat transfer conditions and electrical circuit conditions.

In this phase of the test program primary interest has been couple testing, however, testing of single pellets must preceed the proper design of couples. Thus whenever pellet tests have been performed or are in progress, they will be indicated as such and correlated to the final couple.

In order to properly evaluate the performance of couples it is necessary to have a test system which will provide accurate results as well as to be able to accommodate a representative sample and test it under a specified range of conditions. For this reason, a number of devices has been designed and is discussed in the following paragraphs.

Test Equipment

Single Couple Efficiency Tester

A test set-up was designed for measuring the thermal input power and electrical output power of single thermoelectric couples. The design was chosen for easy and rapid assembly and disassembly of the test thermocouples and for simple testing techniques to minimize the lapse between the time of thermoelectric couple fabrication and the time of performance evaluation.

The tester is shown in Figure #1. Heat is supplied to the test couple from an electrical heater and rejected to two cooling blocks which are soldered directly to the cold caps of the couple. Springs placed on each leg of the couple keep the thermoelements under compression to assure good thermal contacts. The couple and the heater are surrounded by thermal insulation which is contained by a guard heater block. A temperature controller maintains the guard heater block at the same temperature as the couple heater block in order to minimize thermal leakage from the thermoelectric element and the couple heater. The guard heater is surrounded by more thermal insulation which is enclosed by an outer container. Heavy braids connect the cooling blocks on the thermoelectric couple to the electrical load and instrumentation. The efficiency values are obtained by measuring thermal power input, heat exchanger dissipation, and electrical power output.

Multicouple Efficiency Tester

The multiple couple efficiency test fixture, Figure #2, is designed to measure couple thermal power inputs, electrical power outputs, voltages, resistances, and temperatures. The fixtures can accept as many as eight thermocouples arranged to closely approximate a generator module. A variety of module sizes can be accommodated.

The test rig contains a guard heater to minimize heat leakage from the couple heater. The heat sink consists of both heaters and water coolers to provide a wide range of heat sink temperatures. The gases around the fixture can be evacuated under the bell jar to reduce heat leakages.

Single Couple Life Test Modules

Test fixtures of this type were designed for long time operation, with the added features of controlling internal gas pressure and composition. Provision for water cooling of the plate has also been made. An insulated heater block is placed at the center of the plate on top of which the thermoelectric couple is placed and soldered to the heavy power output braids. On top of the couple hot side a lava block with another heater block is placed and the assembly compressed to provide good thermal contact. A metallic enclosure with a sealed side window is then placed on top of the plate over the couple assembly, and the final seal provided by an "O" ring placed in the groove of the plate and compressed by the flange of the metallic container.

Electrical power output, heat input, etc., can be obtained in the same manner as on previously described test set-ups. Cycling is provided by timing devices external to the test fixtures, Figure #3.

Multi-Couple Life Test Modules

The basic design of this type of test assembly is the same as the single couple test rig previously described except that it is able to accept up to 8 thermoelectric couples. Instrumentation of this type of module is installed in such a way as to monitor each couple separately as well as the whole assembly. Figure #4 shows the life test modules.

In addition to the modules in which atmospheric conditions are controlled, special assemblies are used for in-air tests. These are much simpler in their construction, consisting of a heater block on the hot side, thermoelectric couple ladder, a water flow heat exchanger on the cold side, and the temperature instrumentation.

Generator Simulator Test Fixtures

These fixtures provide great flexibility to produce any combination of the following variables in special test modules:

1. hot side base material - steel, aluminum, etc.
2. hot side coating - glasses, ceramics, etc.
3. material to produce a good thermal contact between hot side coating and hot strap of couple.
4. thermoelectric couple.
5. encapsulation.
6. thermal insulations.
7. materials to produce a good thermal contact between cold strap of couple and cold side coating.
8. cold side coating - glasses, ceramics, etc.

9. cold side base material - steel, aluminum, etc.

10. surrounding atmosphere - argon, helium, etc.

Information can be obtained on the interaction of all of the variables, providing valuable data for module design including power output values and life of a thermoelectric generator.

The test fixtures are designed to fit inside of a bell jar. They consist of an insulated heater block for heating the hot side base material, a cold side heater block which is also provided with water cooling to produce a wide range of temperatures on the cold side base material, a vacuum discharge line, a gas charging line to provide the desired atmosphere, thermocouples and power output, electrical feed throughs, and water cooling lines.

These fixtures may be used to determine:

1. the electrical output and lifetime of the thermoelectric couple.
2. the electrical resistance of various hot and cold side coatings plotted against either temperature or time.
3. the thermal drops occurring across the interfaces between the thermoelectric couple and the hot and cold side coatings.
4. the dielectric strength of the core coatings plotted against either temperature or time.
5. chemical reactions which occur among the couple, encapsulations, core coatings, and thermal insulation.

Four test fixtures (Figure #5) for generator simulator tests are available. Additional information on test equipment is in Appendix A.

Module Description and Test Results:

A total of 45 module assemblied containing various couple designs and operating under different conditions are now on test. Of the above tests there are; 1) 10 single couple tests in air, 2) 2 four couple module tests in air, 3) 15 single couple tests in hydrogen argon atmosphere, 4) 17 four couple tests in hydrogen argon atmosphere, and 5) 1 eight couple module operating in a nitrogen atmosphere. The hot strap temperatures vary from 400°C to 550°C with a cold strap temperatures ranging from 40° to 170°C. Since new tests modules are continuously being put on test the time of operation ranges from 100 hrs. to 15000 hrs.

The following paragraphs give a brief description of representative test modules. Their performance results are shown in the respective graphs.

Module EP-3 consists of 8 PbTe-GeBiTe couples (designated as TAP-100F couples) with N and P leg dimensions of 1/2" diameter x 1/2" high. These couples are an early "State-of-the-Art" couple and have a performance factor of 0.94.* The module was assembled using phlogopite mica as hot and cold side electrical insulation, potassium titnate thermal insulation and a resin coating on the thermoelements. The module has been thermally cycled for a total of 20 cycles to date. Total time of operation 9500 hrs. Figure #6.

---

*A factor obtained by comparing any individual modules performance to the performance that could be obtained from a module assembled with the highest performance, TAP-100F type couples at the same operating temperature and geometries.

Module X-1 consists of four PbTe-GeBiTe couples (1/2" diameter x 1/4" high legs) and has a performance factor of 0.77. The couples in the module were fabricated using Sn diffused contacts on the thermoelements. The module has been cycled at approximately one thermal cycle per week. At the end of 4400 hrs. the module was transferred to the Naval Engineering Experimental Station where tests are being continued.

Module X-2 consisted of four PbTe-GeBiTe couples (1/2" diameter x 1/2" high legs) with performance factor of 1.27. Couples in this module were fabricated using a bi-metallic hot strap of silver and cobalt in an effort to match the thermal expansion of the hot strap to the T. E. material. This module was disassembled at the end of 3000 hrs. due to rapid degradation.

Modules X-3 and X-4 are the same as X-2 with performance factors of 1.22 and 1.17 respectively. Figures #7 and #8 show test results.

Module X-5 consists of four latest modified TAP-100F couples and has a performance factor of 1.17. Thermal cycling is at a rate of approximately one thermal cycle per week. This module was also transferred and is being tested at the Naval Engineering Experimental Station. At the time of transfer the module had operated a total of 4100 hrs.

Module X-9 consists of four PbTe-GeBiTe couples and is similar to Module X-1 except that pellet dimensions are 1/2" diameter x 1/2" high. Module assembly consists of phlogopite mica and "hard coated" aluminum as the hot and cold side electrical insulation. The module is being thermally cycled at approximately one cycle per week. Figure #9.

Module X-12 consists of four PbTe-SbBiTe couples. Pellet dimensions are 1/4" x 1/4" x 1/2". The couples were fabricated on a silver hot strap with a gold-indium alloy used as the hot side joining material and tin as the cold side joining material. Figure #10.

Module X-13 consists of four PbTe-SbInTe couples. Pellet dimensions are 1/4" x 1/4" x 1/2". The P-leg contact is made by the use of plasma sprayed Fe and a flash of Ni for wetting purposes. The N-leg contact with plasma sprayed Co and a flash of Ni. Module hot side is operating at 425°C. Data is given in Figure 11.

Module X-15 is the same as Module X-12 except the pellet dimensions are 1/4" x 1/2" x 1/4". Test data is given in Figure #12.

Module X-20 consists of four GeBiTe-PbTe couples. Contacts were made by a Sn diffusion process. The P-leg is 1/2" diameter x 3/8" high. The N-leg is 1/2" diameter x 1/4" high. Hot straps are made from stainless steel. Module is operating at a hot side temperature of 500°C. Data is given in Figure #13.

Module XD-1 consists of one PbTe-N-PbTe-P couple, with pressure contact joint on the hot strap (iron) and Sn joints on the cold side. Pellet dimensions are 1/2" diameter by 1/4" high. This type of couple assembly has proven to have rather fine cycling properties. Test results are given in Figure #14.

Module XD-3 is the same as Module XD-1 except four couples have been assembled. This module is being cycled 6 times per day. Data is given in Figure #15.

Couple #6476 is a TAP-100F type couple. P-leg GeBiTe 1/2" diameter by 1/2" high. N-leg PbTe 1/2" diameter by 1/2" high. The couple is running in air with a nominal amount of cycling. It has a silicone resin coating on pellet surfaces. Total operating time is 12400 hrs. Test results are given in Figure #16.

Measuring the efficiency of thermocouples and modules requires a great deal of time, patience, care, and well designed equipment. Much effort has been given to this aspect of the program. Two vacuum and inert gas type efficiency checkers and several atmospheric type measuring systems have been developed with accuracies suitable for the Module Improvement Program. The testers have been described previously.

Since efficiency tests are rather lengthy and only two vacuum type testers are available, only selected couple systems can be checked. Efficiency data on most of the previously discussed couples has been obtained and was

discussed in detail in previous reports.

Additional and more specific discussions on couple testing are presented in Appendices B and C.

Conclusions

The highest module efficiencies are achieved at low heat flux densities. As heat flux density is increased in an attempt to reduce generator size, the efficiency is reduced. This loss in performance is caused primarily by thermal and electrical contact resistances inherent in any module system. In designing a module for minimum size or maximum efficiency, the heat transfer characteristics of the heat source, the heat sink, and the module must be considered from a system aspect.

A thermoelectric generator can be defined as a heat engine in which heat enters at a relatively high temperature, and is rejected at a lower temperature. A percentage of the heat that passes through the generator is converted to electrical energy. The d-c output voltage is approximately proportional to the difference in temperature between the heat entering and the heat rejected by the generator. The rate at which heat can enter the generator, and consequently the electrical power that can be generated, is determined by the rate at which the generator heat sink can reject heat. The electrical power generated is determined by the product of the efficiency of the generator times the rate of heat flowing through the generator.

The thermoelectric generator is composed of one or more thermocouples made up of P- and N-legs connected in series by an electrically conducting

material. All thermoelements in a single stage generators are connected in parellel in the heat flow circuit. A module is a discrete section of a generator -- an independent structure or enclosure that houses one or more thermocouples. This basic module concept may, in practical form, appear in a variety of shapes and sizes. Among the many geometries that have been considered are thermoelements that are rectangular, round, washer shaped, concentrically mounted, and multi-column. However, despite the shape of the thermoelements, there are many common factors that determine the performance and characteristics of a module.

There are two important factors that limit the power generating capability of a module. The first factor, thermal contact resistance, degrades generator efficiency by introducing irreversible losses into the heat flow circuit. It is one of several obstacles that inhibits reduction in generator size and reduces generator efficiency. The second factor, electrical resistance, degrades generator efficiency by introducing resistance in the series electrical power circuit. This resistance also increases the irreversible losses in the system and limits the reduction in thermoelement length that can be achieved.

The thermoelement area, length, and shape are restricted by mechanical stresses in the bulk material caused by the temperature difference between the hot and cold sides. Additional stresses can arise due to differences in coefficient of expansion between the thermocouple legs and the connecting strap. Also, consideration must be given to the stresses introduced into the thermo-

couples by the expansion and contraction of the module structure as it passes through cycles of heating and cooling. The structure design problem is compounded by the requirement that the hot and cold walls of the module maintain good thermal contact with the respective hot and cold straps of each thermocouple.

Once a thermocouple design has been finalized, it will have a characteristic efficiency that is determined by thermoelement material characteristics, compatibility between the various materials, contact resistance, the degree to which the design has been optimized, and operating temperatures. Major changes in thermocouple length, area and shape have been found to influence the performance of the thermocouple. Contact resistance and internal stresses in the thermoelements presently limit the heat flux densities at which thermocouples can effectively operate.

Calculations indicate that couples which are long in the direction of heat flow compared to the cross sectional area will tend to have smaller stresses than those that are shorter in the direction of heat flow, thus indicating better overall performance and longer life. Practical evaluations, however, have shown contrary to the above. As an example couples assembled with 1/2" diameter 1/4" high pellets have been shown to perform better from the standpoint of cycling and life that those manufactured from 1/2" diameter 1/2" high pellets. This can be attributed to manufacturing conditions. When using a powder pressing process to form pellets, it was found that the 1/4" high pellet was mechanically stronger and more homogeneous than pellets of greater height.

When operated in a module, the performance of thermocouples is degraded by the following factors:

1. non-uniform temperatures on the hot and cold sides of the module.
2. Temperature drops that appear across the hot and cold thermal contacts of the couple and across the flexible braids if they are used.
3. heat that leaks past the thermocouple through the thermal insulation, the encapsulation material, and the sealing plates.

The cumulative effect of the above factors for heat fluxes of 30 watts/in^2 can lower the effective efficiency of a thermocouple 10 to 20 percent in a generator.

Extensive development programs, however, have minimized the above described degradation factors. Temperature distribution has been improved to the extent that a 5°C gradient can be obtained over a one square foot area and 30°C gradients over areas up to 12 ft^2 with standard gas or liquid heat sources. Temperature drops and heat leaks have been minimized with better assembly techniques and improved insulations respectively. As a result of these improvements and the continued development of improved couples, considerable increase in the overall performance of modules has been observed. Single couple operation has exceeded the 15000 hr. mark. Test modules have operated in excess of 10000 hrs. with less than 25% degradation and an increase rate of cycling. The average module life has increased about 5000 hrs. in the last two years from 2500 hours to 7500 hours.

Figure 1 Single Couple Efficiency Tester

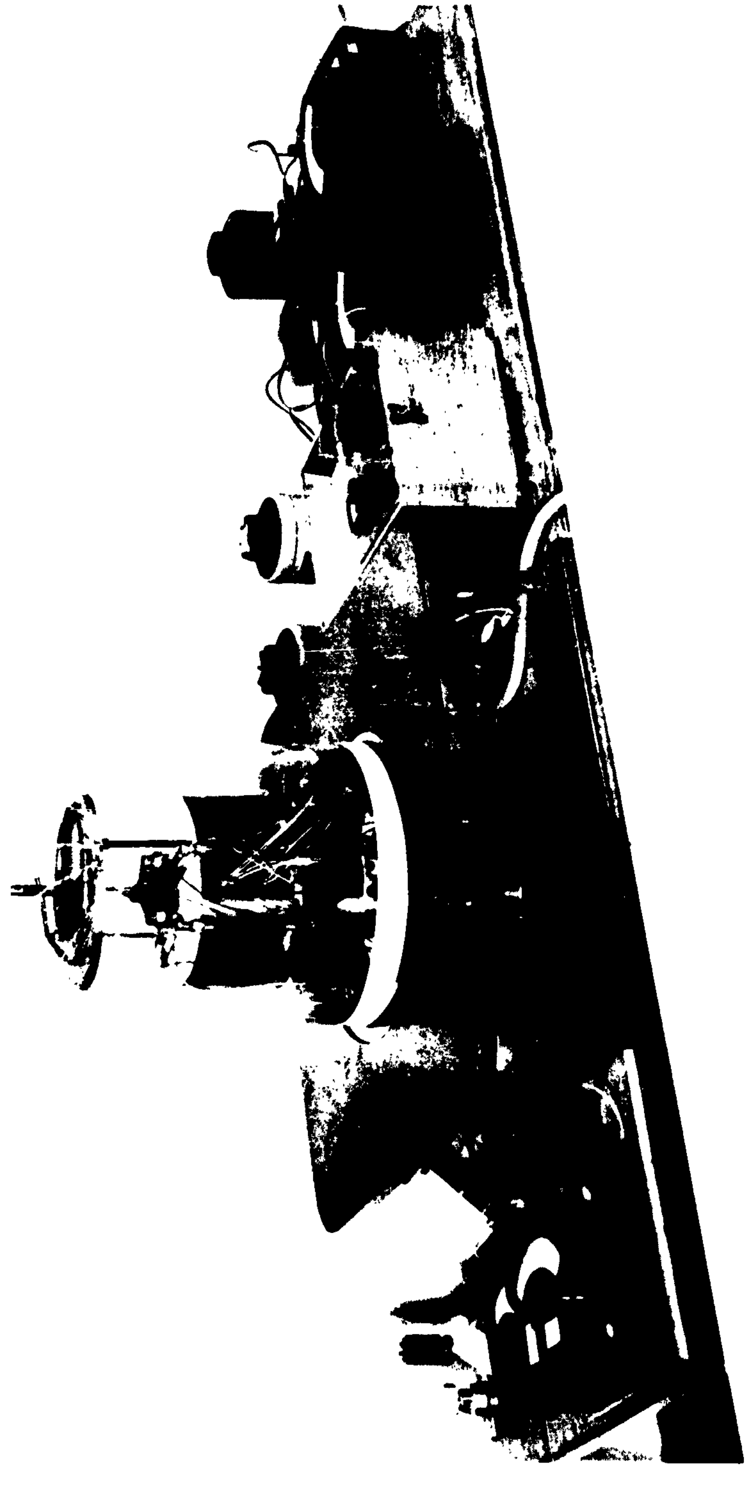


Figure 2   Multi Couple Efficiency Tester

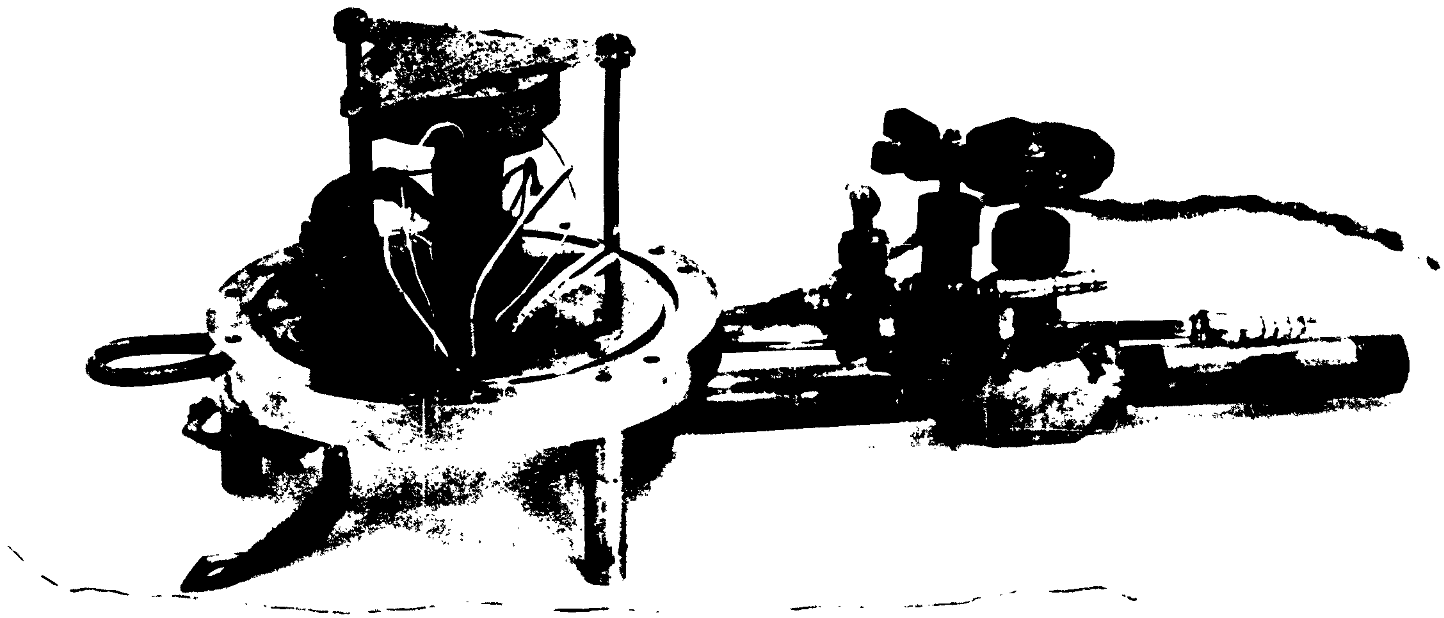


Figure 3 Single Couple Life Tester

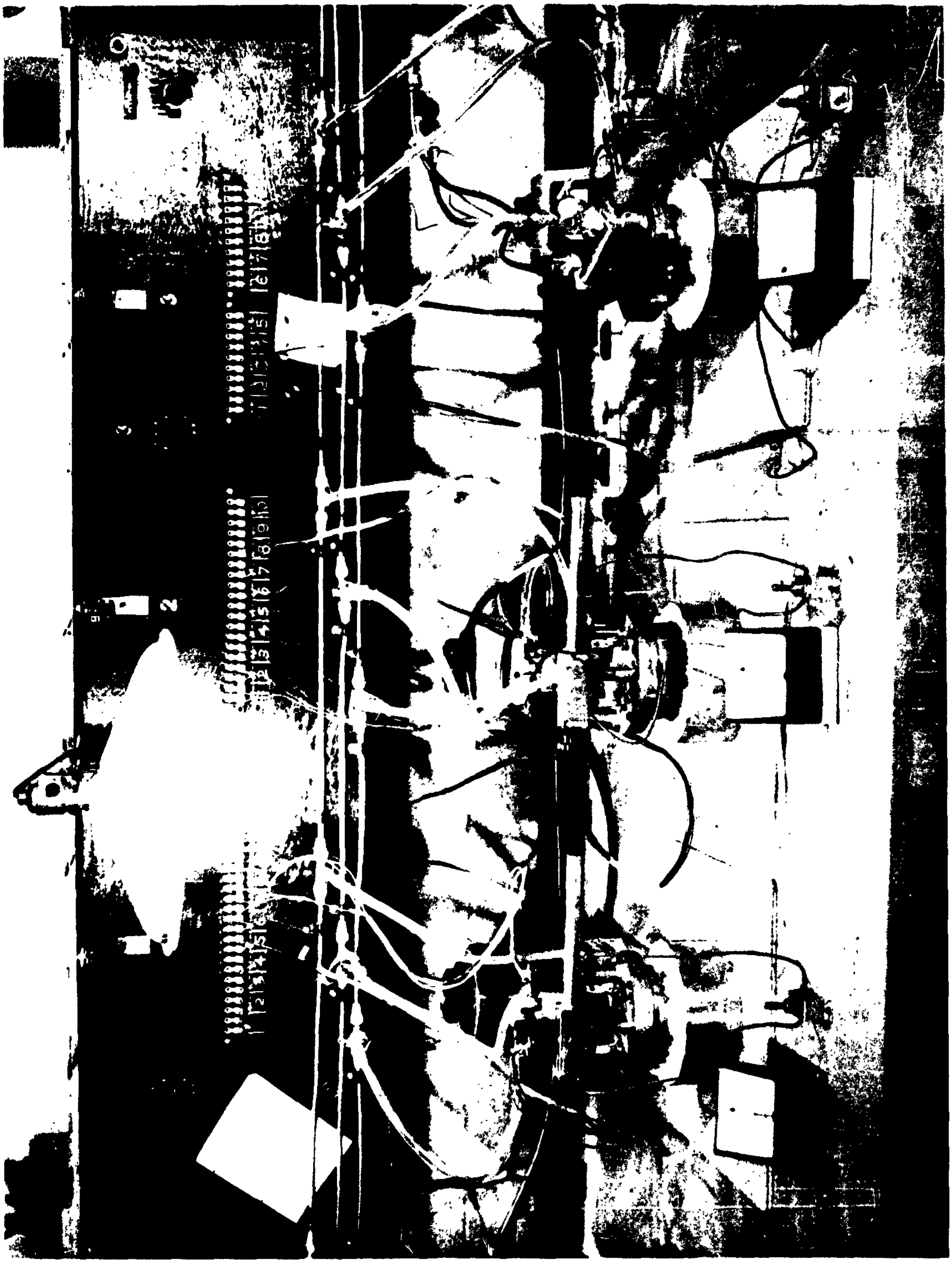


Figure 4 Multi Couple Life Testers

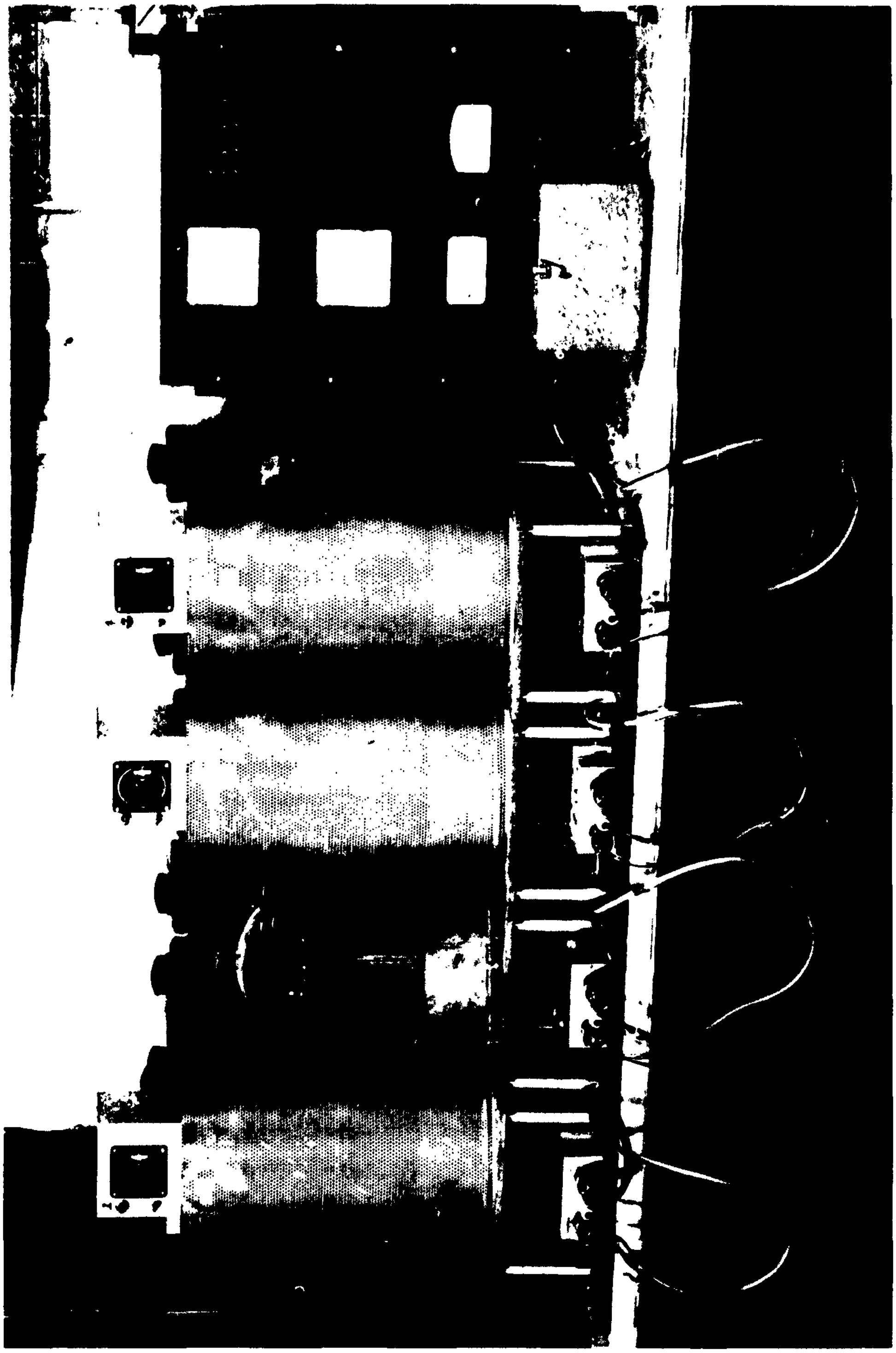


Figure 5 Generator Simulator Testers

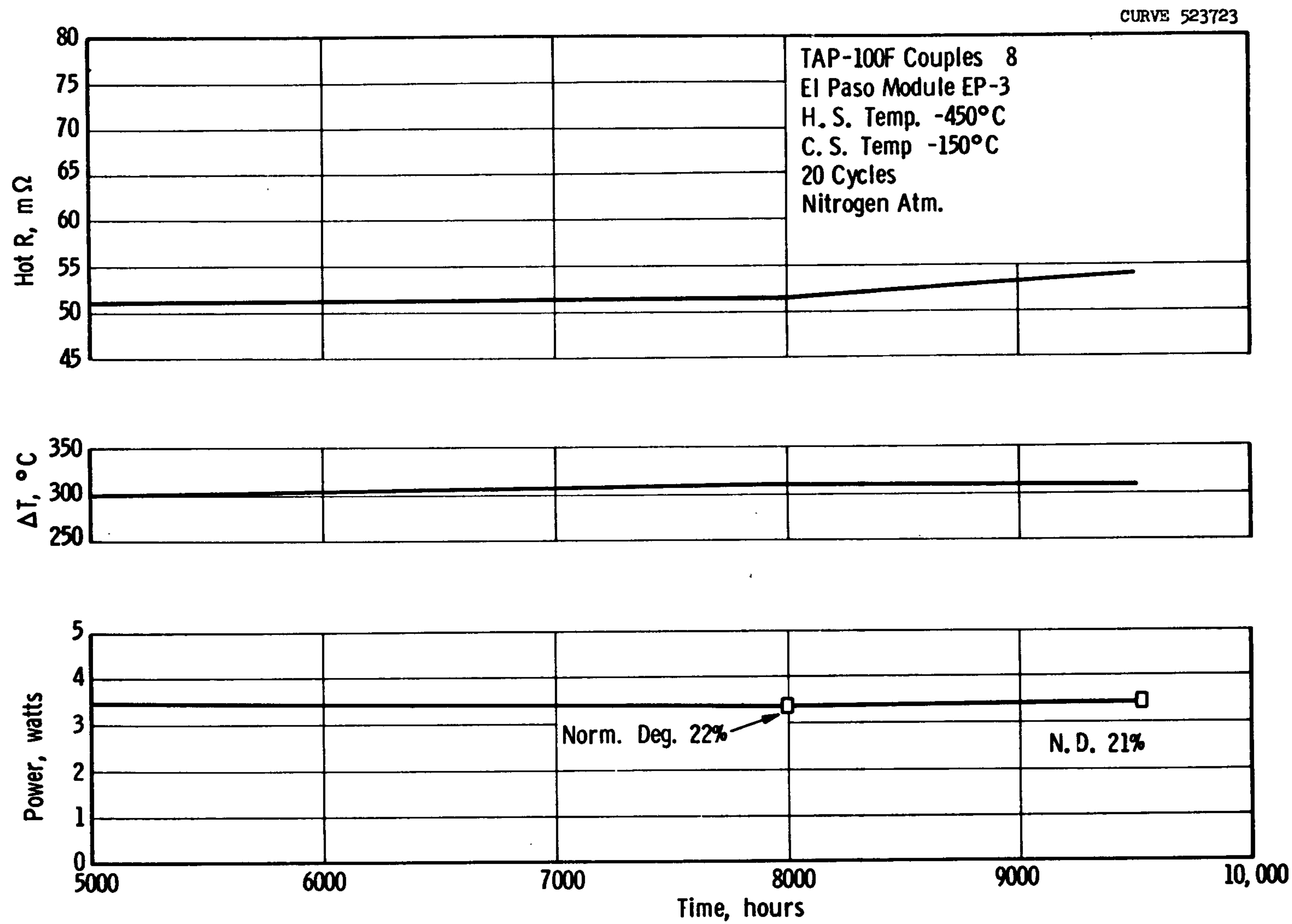

CURVE 523723
TAP-100F Couples 8
El Paso Module EP-3
H. S. Temp. -450°C
C. S. Temp -150°C
20 Cycles
Nitrogen Atm.
Hot R, mΩ
80
75
70
65
60
55
50
45
ΔT, °C
350
300
250
Power, watts
5
4
3
2
1
0
Norm. Deg. 22%
N. D. 21%
5000
6000
7000
8000
9000
10,000
Time, hours

FIGURE 6

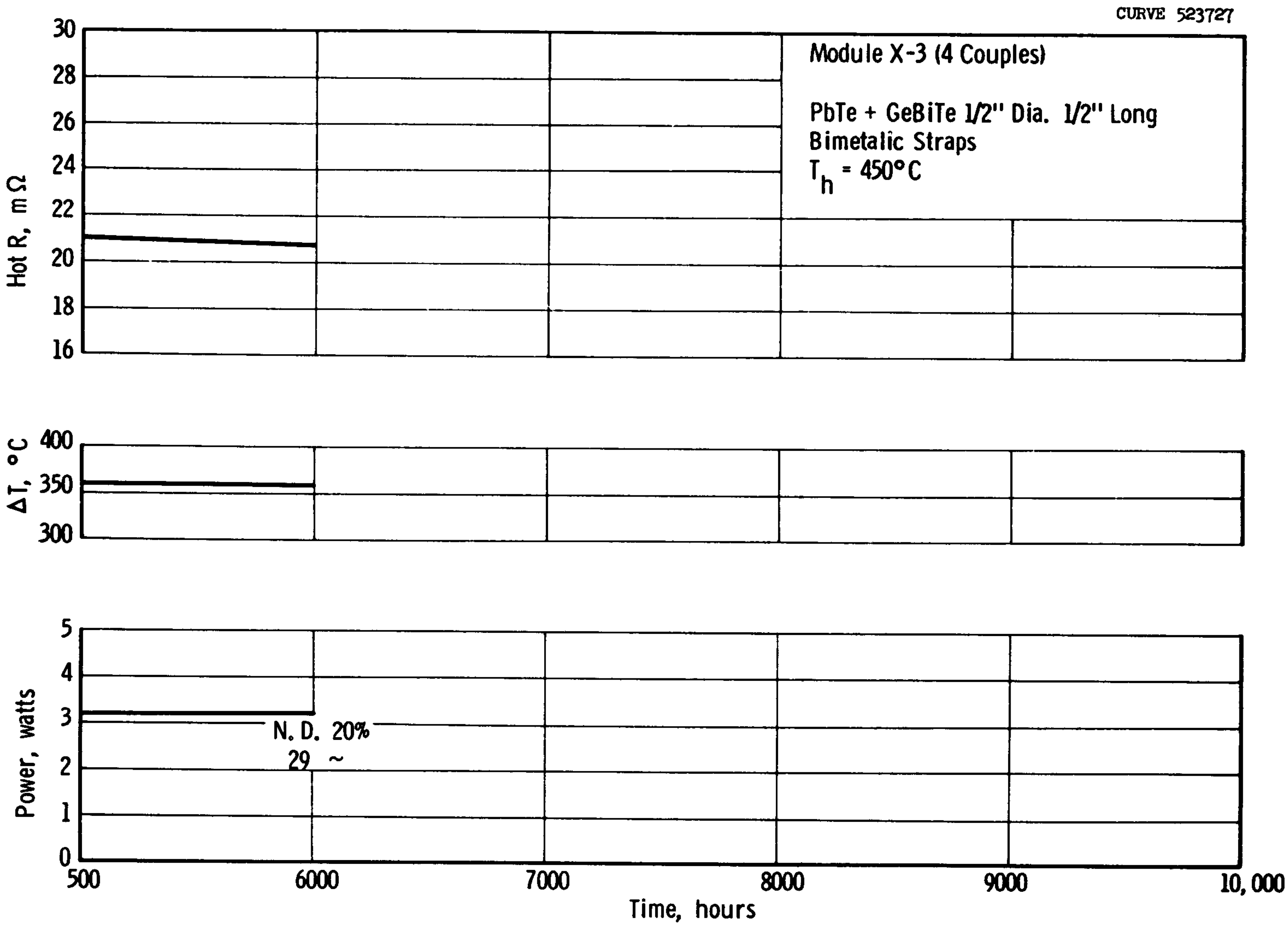
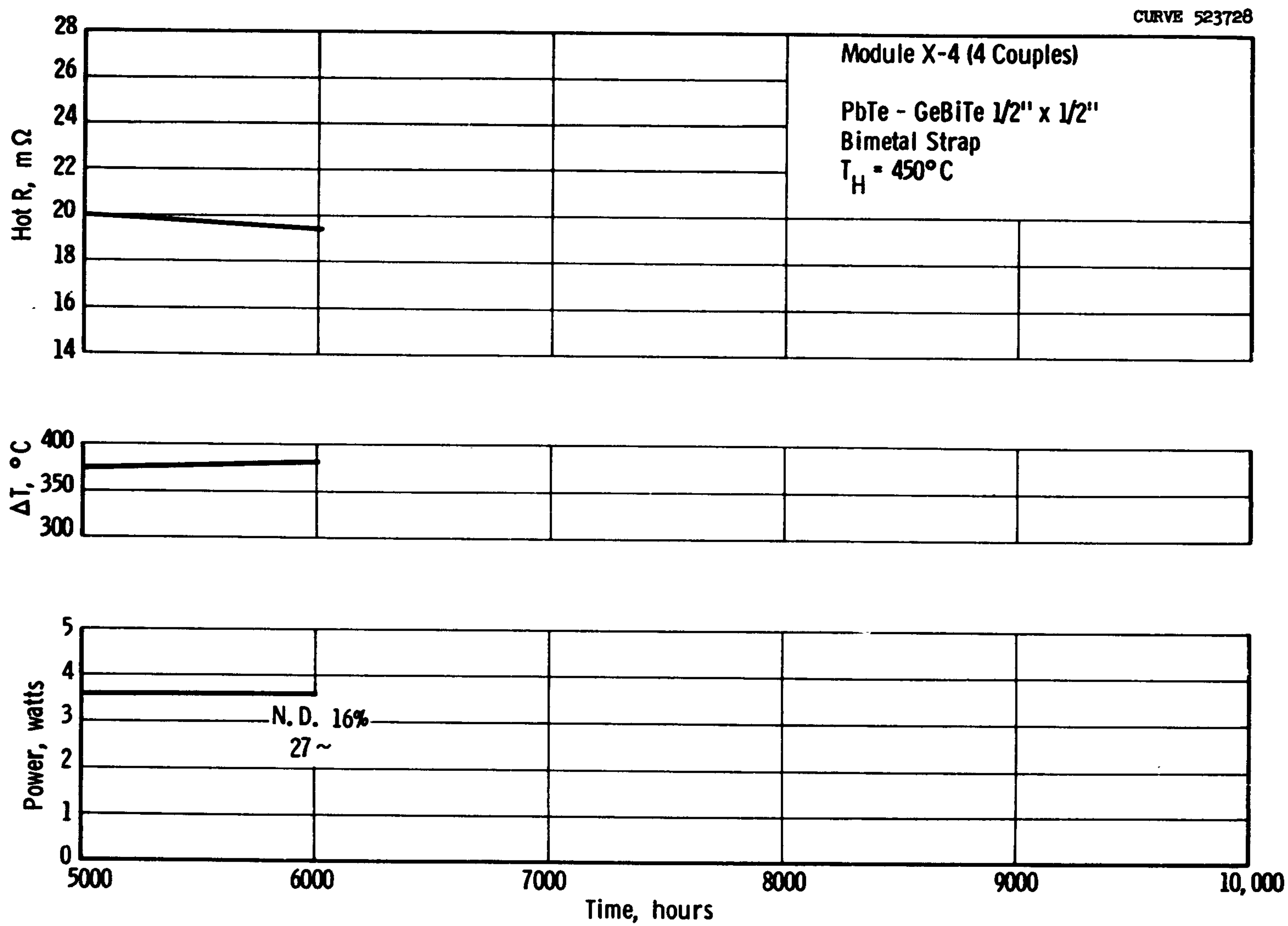

CURVE 523727
Module X-3 (4 Couples)
PbTe + GeBiTe 1/2" Dia. 1/2" Long
Bimetalic Straps
T_h = 450°C
Hot R, m Ω
30
28
26
24
22
20
18
16
ΔT, °C
400
350
300
Power, watts
5
4
3
2
1
0
N. D. 20%
29 ~
500
6000
7000
8000
9000
10,000
Time, hours

FIGURE 7



CURVE 523728
Module X-4 (4 Couples)
PbTe - GeBiTe 1/2" x 1/2"
Bimetal Strap
T_H = 450°C
Hot R, mΩ
28
26
24
22
20
18
16
14
ΔT, °C
400
350
300
Power, watts
5
4
3
2
1
0
N.D. 16%
27 ~
5000
6000
7000
8000
9000
10,000
Time, hours

FIGURE 8

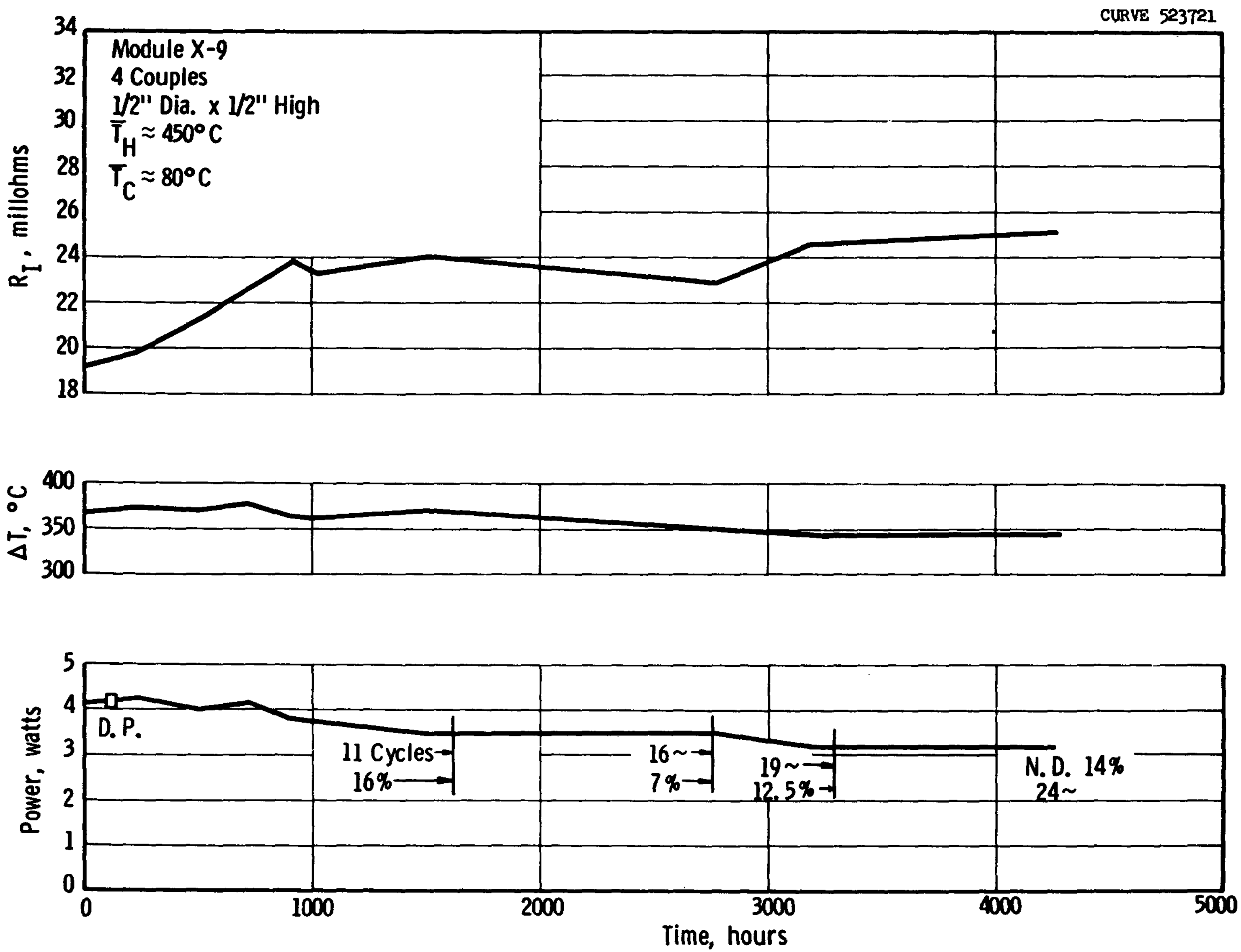

CURVE 523721
Module X-9
4 Couples
1/2" Dia. x 1/2" High
$\overline{T}_H \approx 450°C$
$\overline{T}_C \approx 80°C$
R_I, milliohms
ΔT, °C
Power, watts
D. P.
11 Cycles
16%
16~
7%
19~
12.5%
N.D. 14%
24~
Time, hours
34
32
30
28
26
24
22
20
18
400
350
300
5
4
3
2
1
0
1000
2000
3000
4000
5000

FIGURE 9

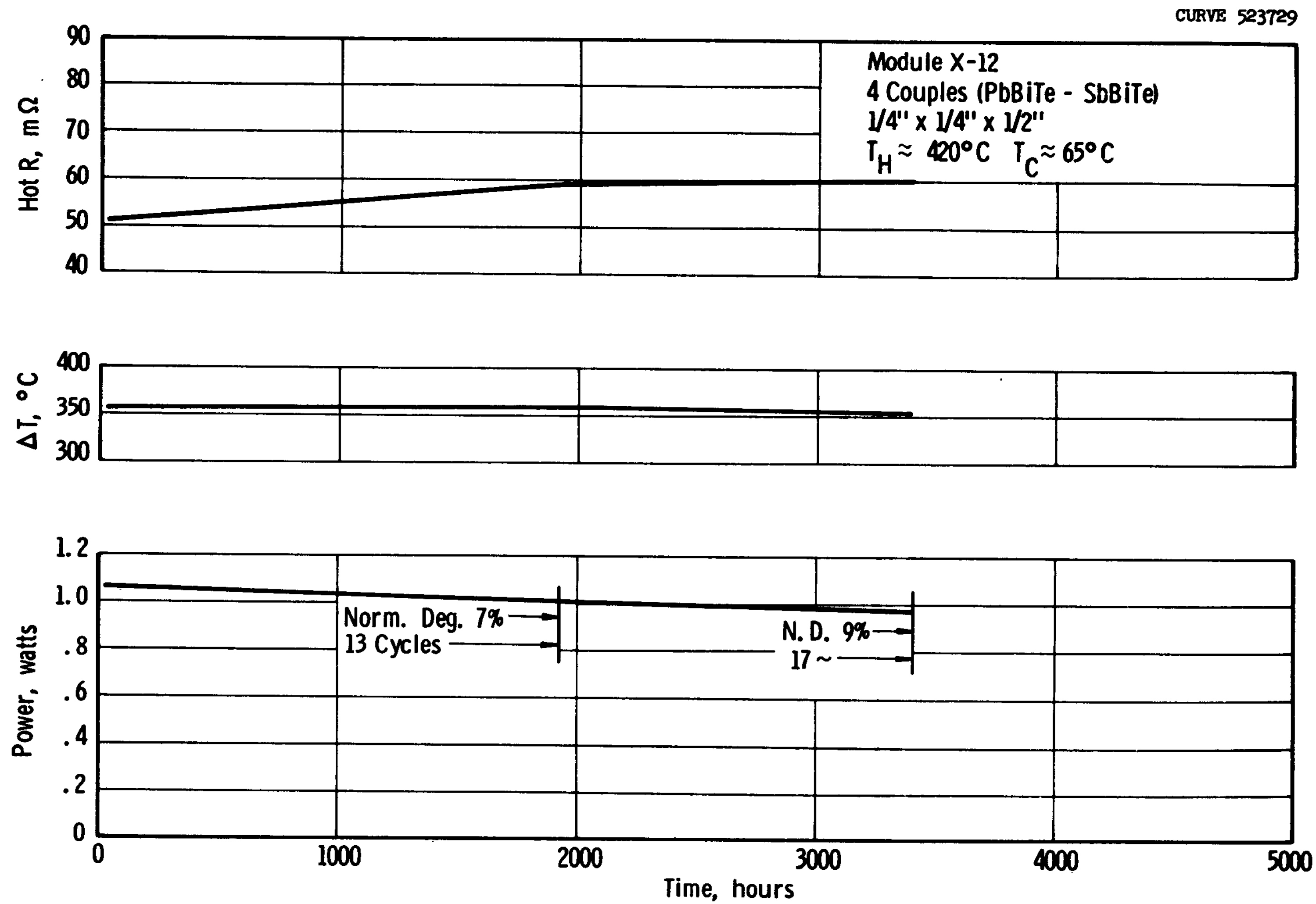

CURVE 523729
Module X-12
4 Couples (PbBiTe - SbBiTe)
1/4" x 1/4" x 1/2"
$T_H \approx$ 420°C $T_C \approx$ 65°C
Hot R, mΩ
90
80
70
60
50
40
ΔT, °C
400
350
300
Power, watts
1.2
1.0
.8
.6
.4
.2
0
Norm. Deg. 7%
13 Cycles
N.D. 9%
17 ~
0
1000
2000
3000
4000
5000
Time, hours

FIGURE 10

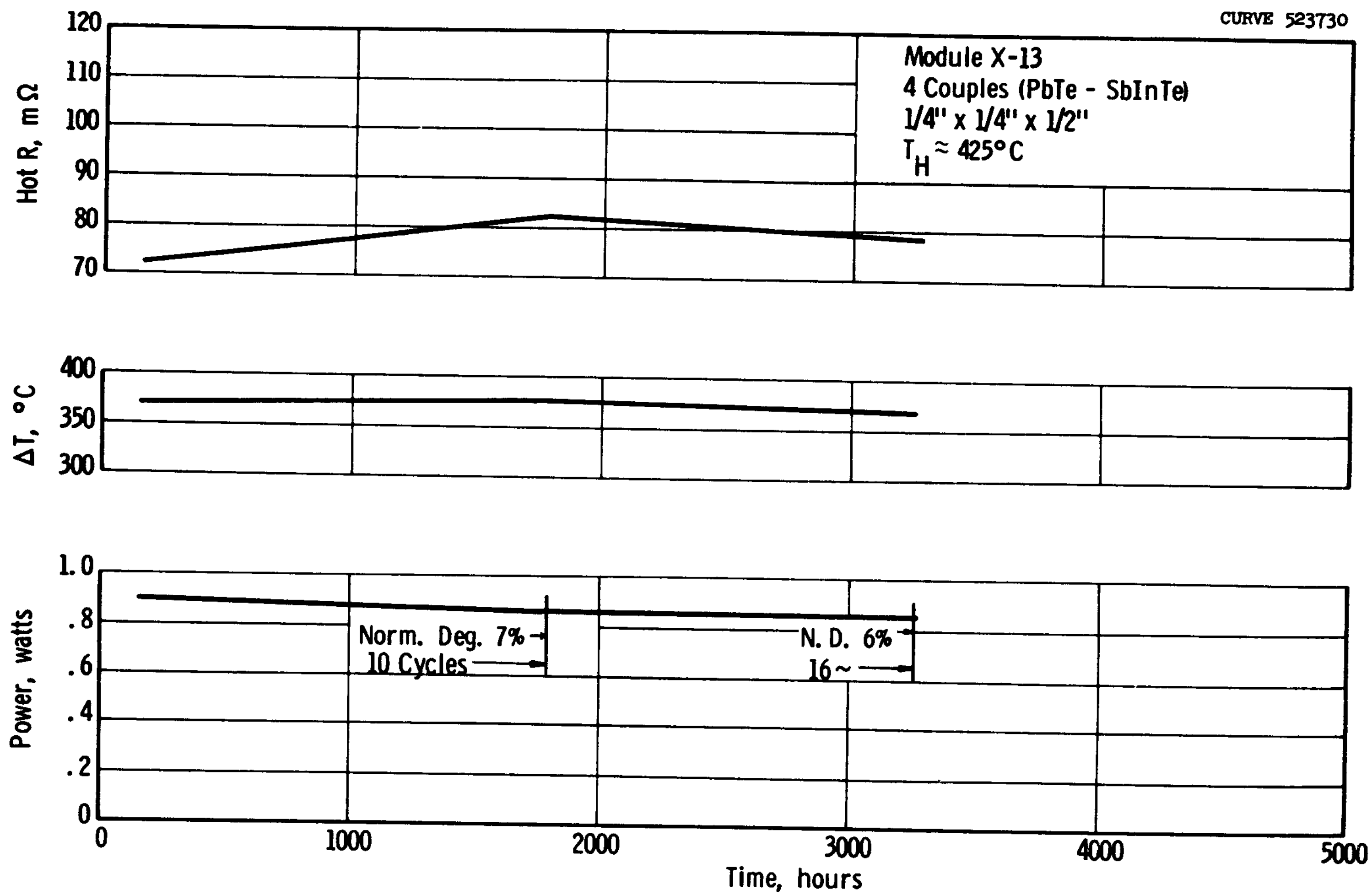

CURVE 523730
Module X-13
4 Couples (PbTe - SbInTe)
1/4" x 1/4" x 1/2"
$T_H \approx 425°C$
Hot R, m Ω
120
110
100
90
80
70
ΔT, °C
400
350
300
Power, watts
1.0
.8
.6
.4
.2
0
Norm. Deg. 7%
10 Cycles
N. D. 6%
16~
0
1000
2000
3000
4000
5000
Time, hours

FIGURE 11

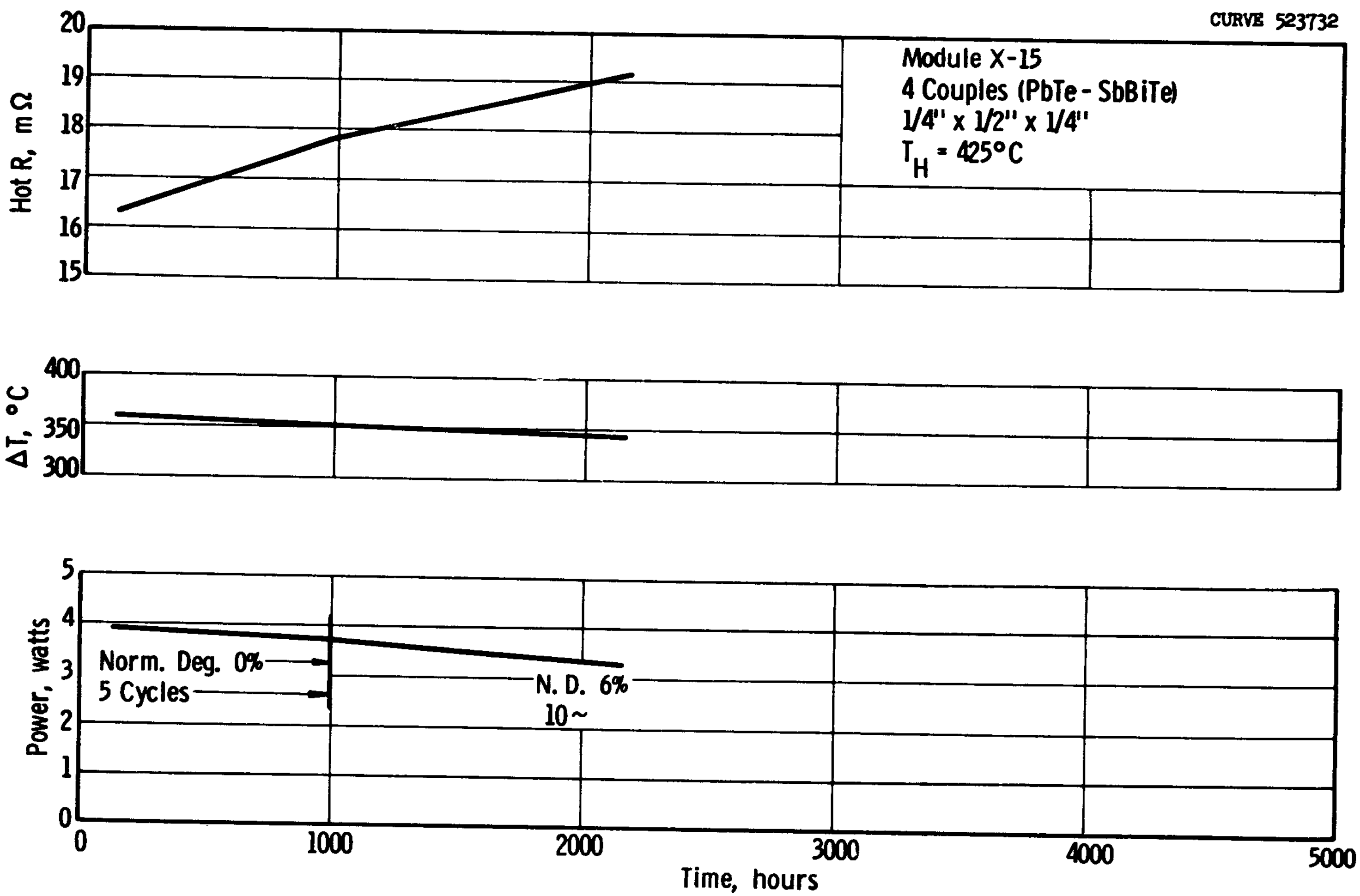

CURVE 523732
Module X-15
4 Couples (PbTe - SbBiTe)
1/4" x 1/2" x 1/4"
T_H = 425°C
Hot R, mΩ
20
19
18
17
16
15
ΔT, °C
400
350
300
Power, watts
5
4
3
2
1
0
Norm. Deg. 0%
5 Cycles
N. D. 6%
10~
0
1000
2000
3000
4000
5000
Time, hours

FIGURE 12

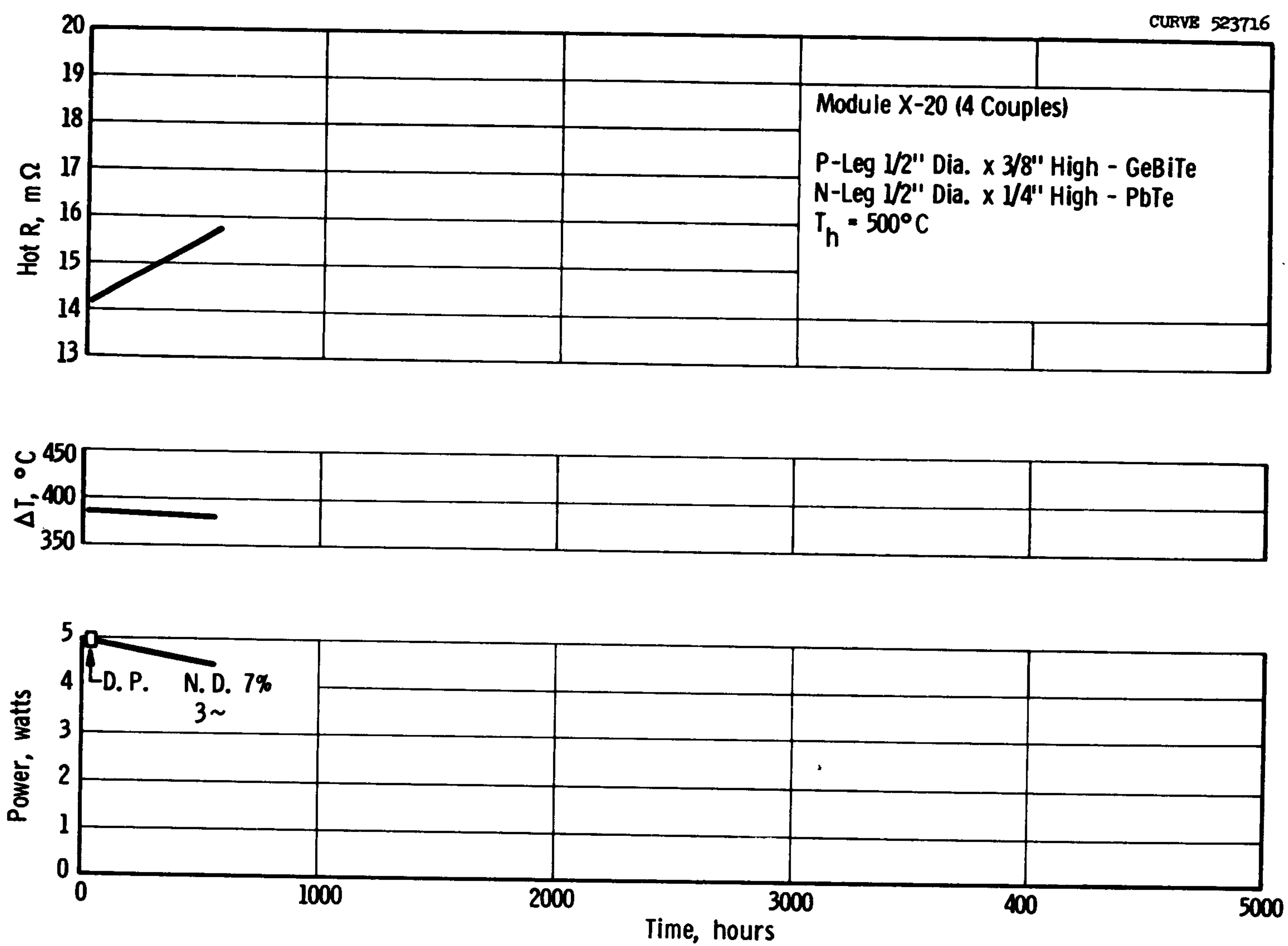

CURVE 523716
Module X-20 (4 Couples)
P-Leg 1/2" Dia. x 3/8" High - GeBiTe
N-Leg 1/2" Dia. x 1/4" High - PbTe
T_h = 500°C
Hot R, mΩ
20
19
18
17
16
15
14
13
ΔT, °C
450
400
350
Power, watts
5
4
3
2
1
0
D.P.
N.D. 7%
3~
0
1000
2000
3000
400
5000
Time, hours

FIGURE 13

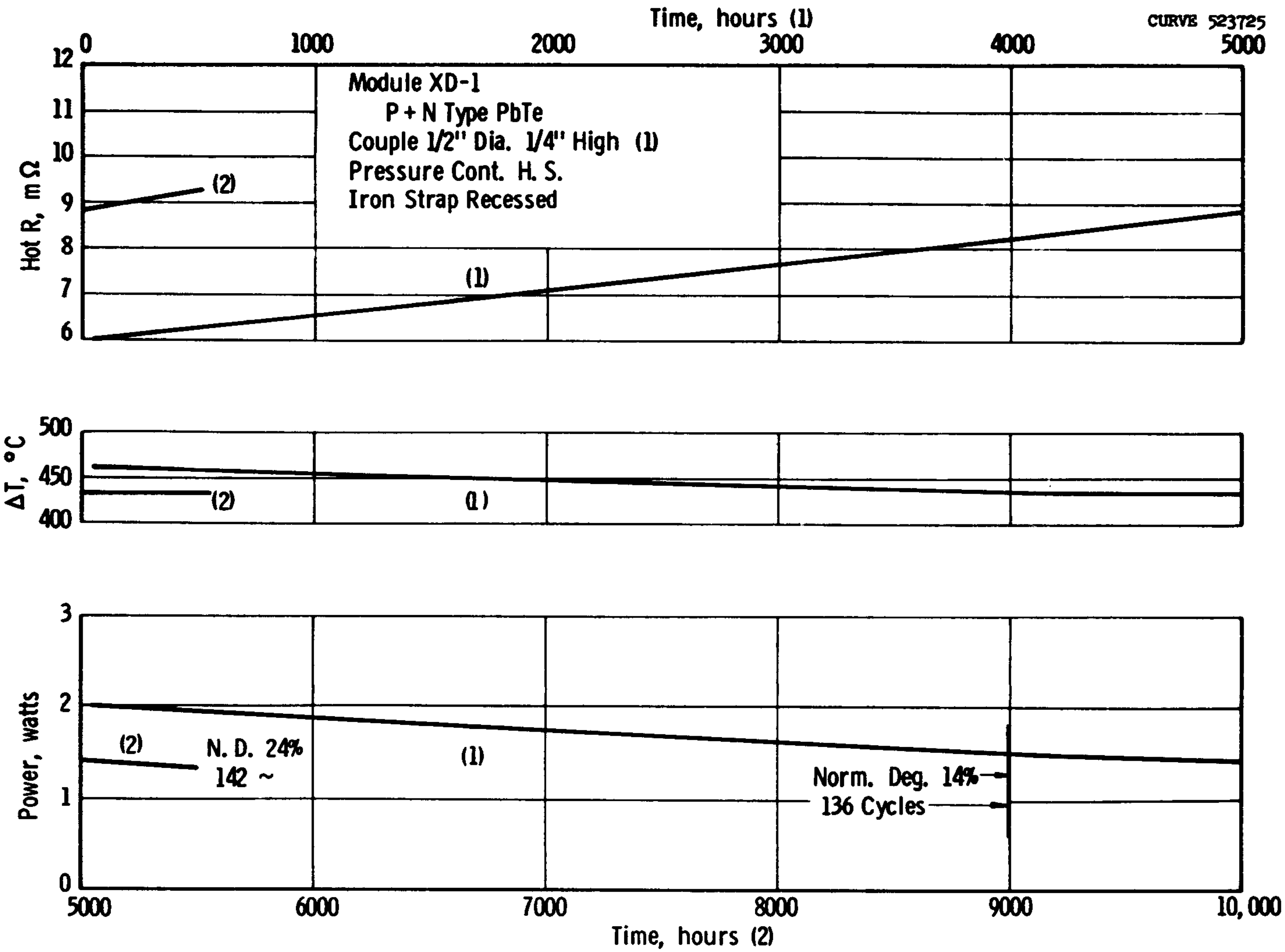

Time, hours (1)
CURVE 523725
0
1000
2000
3000
4000
5000
12
11
10
9
8
7
6
Hot R, mΩ
Module XD-1
P + N Type PbTe
Couple 1/2" Dia. 1/4" High (1)
Pressure Cont. H. S.
Iron Strap Recessed
(2)
(1)
500
450
400
ΔT, °C
(2)
(1)
3
2
1
0
Power, watts
(2)
N. D. 24%
142 ~
(1)
Norm. Deg. 14%
136 Cycles
5000
6000
7000
8000
9000
10,000
Time, hours (2)

FIGURE 14

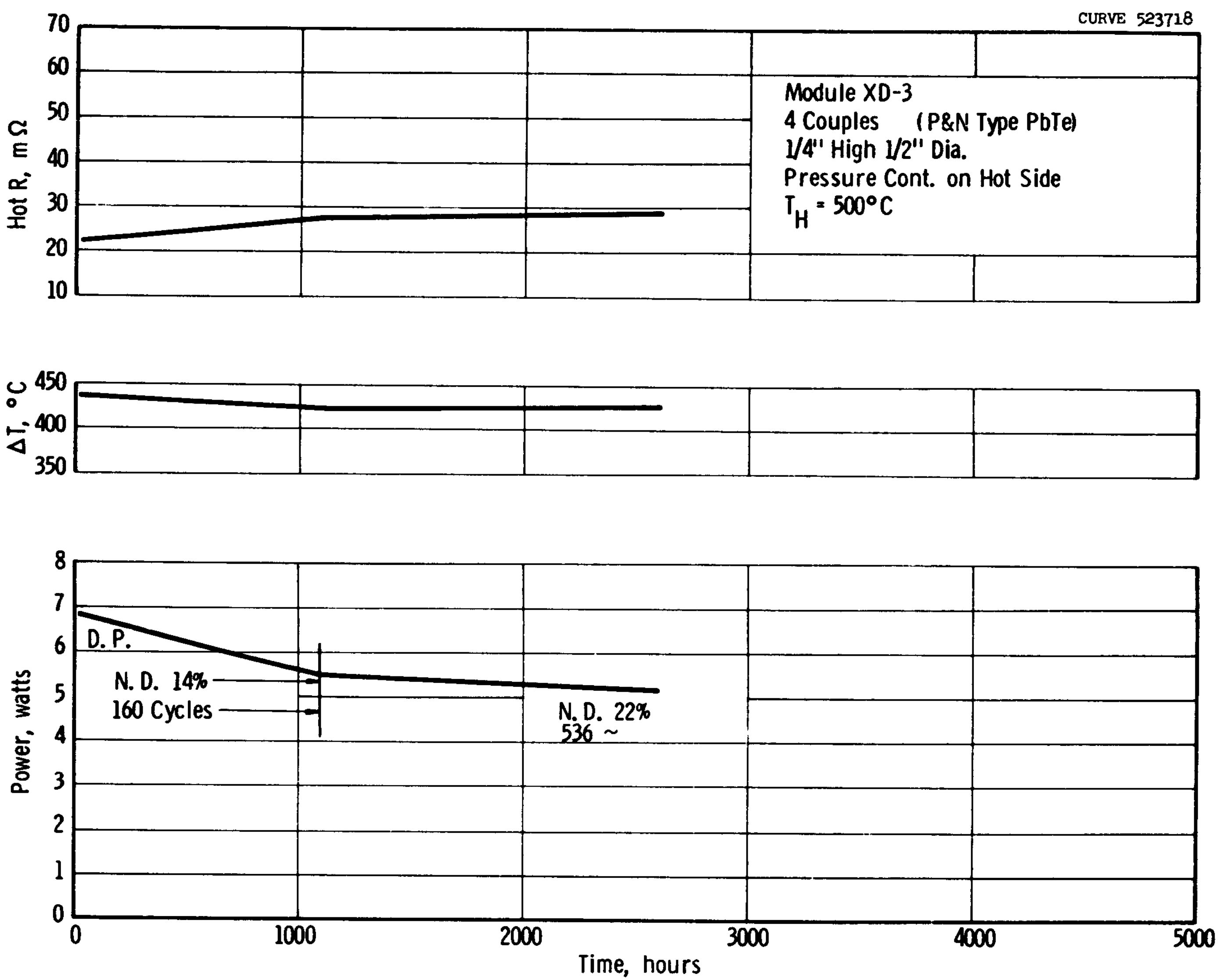

CURVE 523718
Module XD-3
4 Couples (P&N Type PbTe)
1/4" High 1/2" Dia.
Pressure Cont. on Hot Side
T_H = 500°C
Hot R, mΩ
70
60
50
40
30
20
10
ΔT, °C
450
400
350
Power, watts
8
7
6
5
4
3
2
1
0
D. P.
N. D. 14%
160 Cycles
N. D. 22%
536 ~
0
1000
2000
3000
4000
5000
Time, hours

FIGURE 15

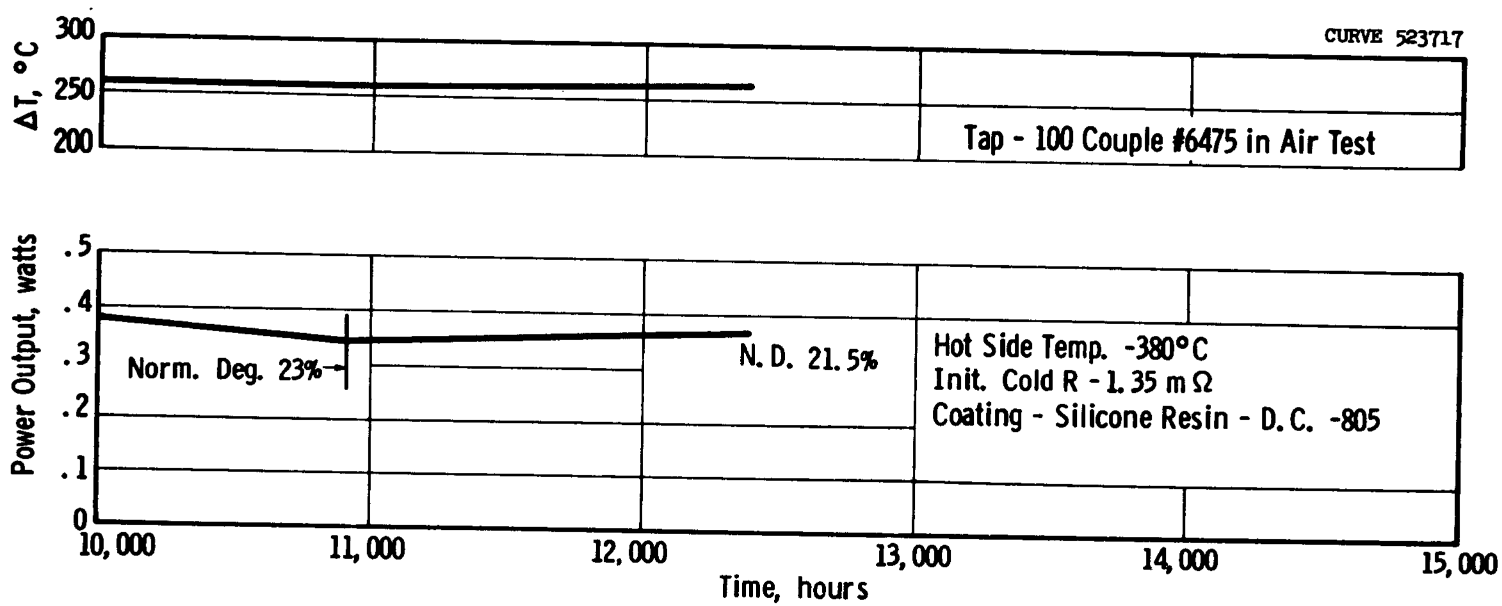

CURVE 523717
ΔT, °C
300
250
200
Tap - 100 Couple #6475 in Air Test
Power Output, watts
.5
.4
.3
.2
.1
0
Norm. Deg. 23%
N. D. 21.5%
Hot Side Temp. -380°C
Init. Cold R - 1.35 m Ω
Coating - Silicone Resin - D. C. -805
10,000
11,000
12,000
13,000
14,000
15,000
Time, hours

FIGURE 16

V. FINAL MODULE FABRICATION AND PERFORMANCE

Three sections of a module having a power output slightly in excess of 30 watts have been built and delivered to the Engineering Experiment Station for life-performance testing. Couples for each of the three sections are different and were chosen on the basis of life-performance testing. A brief summary of each of these module sections and the initial performance follow:

MIP-I PbTe-BiSbTe couple:

This couple utilizes an alternate p material (BiSbTe) developed for power generation use up to a hot side temperature of 425°C.* The relatively small size of the couple makes a rather high heat flux unit. In order to minimize the temperature drop across the braids, large braids, relative to leg cross section, were used. No springs were used; instead the spring action of the braid itself is relied upon. A sketch of the couple is shown in Figure 1, and initial performance data for a 24 couple module section are given in Table 1.

MIP-II PbTe-GeBiTe with hard joints on the hot sides:

The technology for this couple was first developed several years ago. With subsequent improvements in materials and joints, it has become the standard against which other materials and couple fabrication procedures are evaluated. A sketch of this couple is shown in Figure 2. Average properties over the temperature range for the materials used in these couples are as follows:

*Thermoelectricity, Quarterly Progress Report No. 2, August, 1962
NObs 86595

	$\bar{\alpha}$, μV/°C 450°C-100°C	$\bar{\rho}$, Ω-cm x 10^{-3} 450°C-150°C
PbTe	-222	2.15
GeBiTe	+130	1.00

Ten of these couples are mounted in series in the module section. Initial performance data are given in Table I.

MIP-III PbTe-GeBiTe with Sn diffusion joints:

The thermoelectric couples utilized in Module Section No. MIP-III were prepared by means of a tin diffusion technique applied at both the hot and cold junctions. Thermoelectric materials used are pressed and sintered bismuth doped lead telluride for the N-leg and pressed and sintered $Ge_{0.935}Bi_{0.065}Te$ for the P-leg. Dimensions for the N-leg are 1/2 inch diameter by 1/4 inch long and for the P-leg are 1/2 inch diameter by 3/8 inch long. The hot junction strap and the cold junction disks are of 304 stainless steel. All mating faces of both the stainless steel parts and the thermoelectric pellets were ultrasonically wetted with tin and were diffusion bonded before assembly. Diffusion bonding of the tin was performed by heat treatment in argon. The treatment used for tin to stainless steel was 10 minutes at 800°C; the treatment used for tin to germanium bismuth telluride and tin to lead telluride was 10 minutes at 600°C. The hot junction straps were geometrically modified to provide improved resistance to thermal cycling. These couples are intended for relatively high thermal density applications where portability, efficiency and thermal cycling are primary considerations. They are suitable for use over the 500°C to 150°C temperature range for

which they will produce approximately 1.4 watts per couple under matched load conditions. A sketch of this couple is shown in Figure 3, and the initial performance data of the 10 couple module section is shown in Table I.

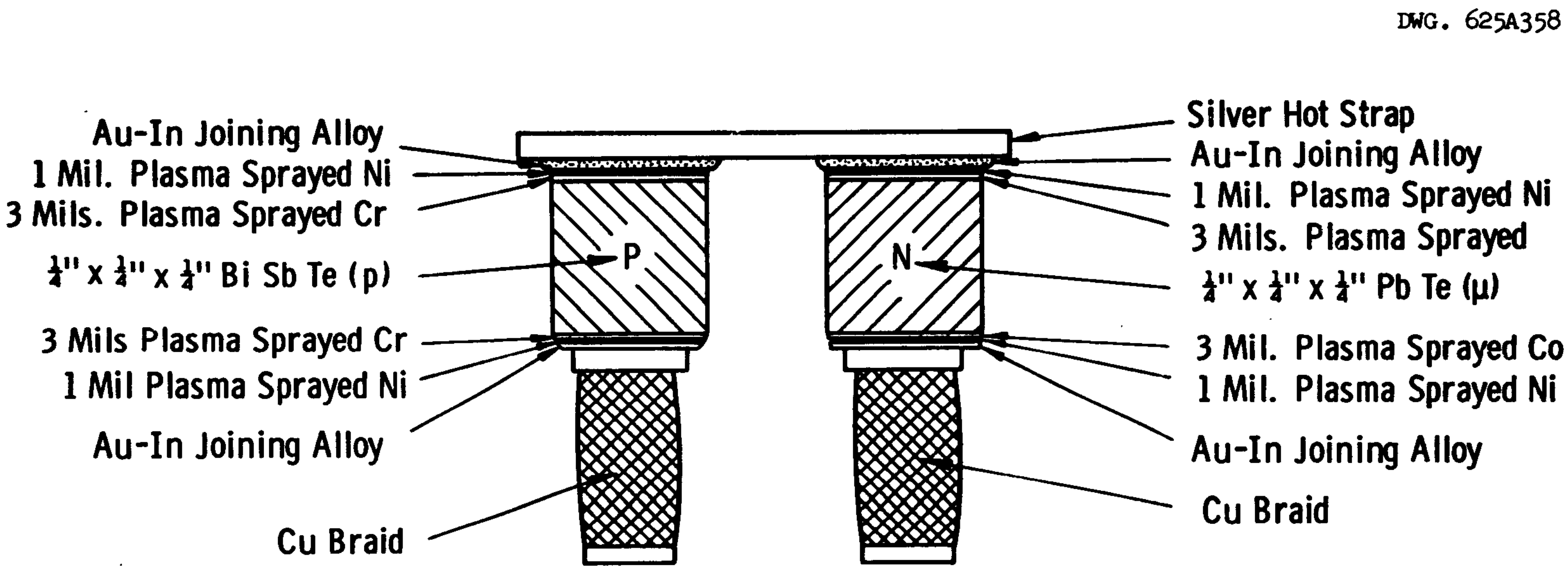


Fig. 1—Pb Te-Bi Sb Te couple, MIP-I

DWG. 625A359

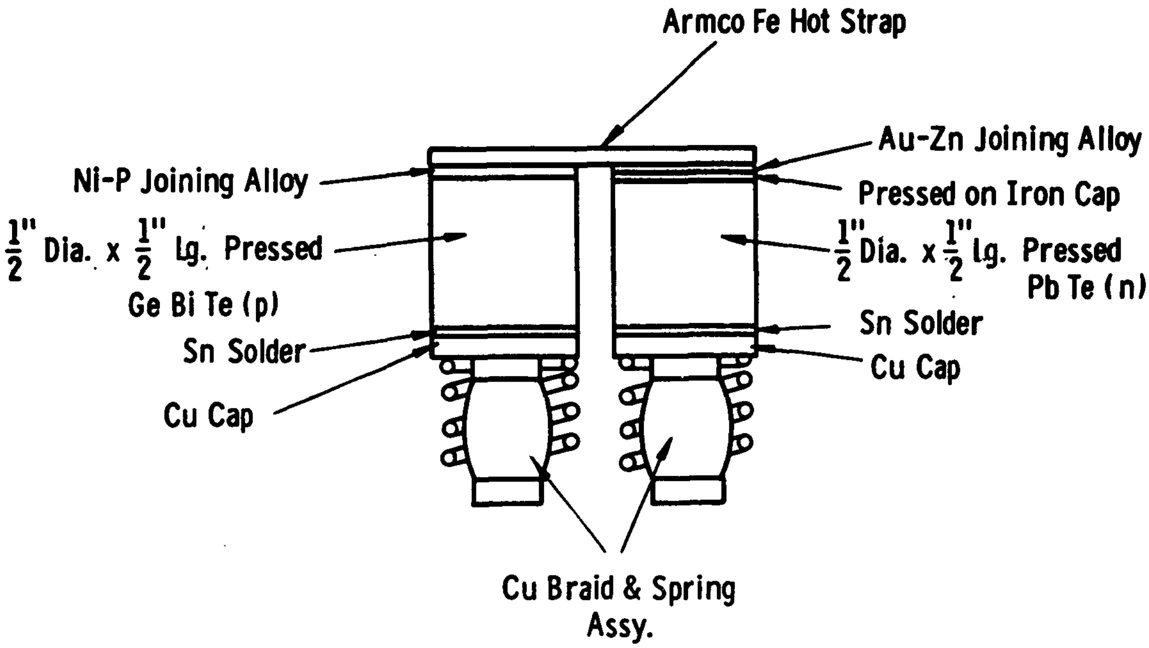


Fig. 2—Pb Te-Ge Bi Te couple with hard joints on the hot sides (Tap-100 style) MIP-II

DWG. 625A360

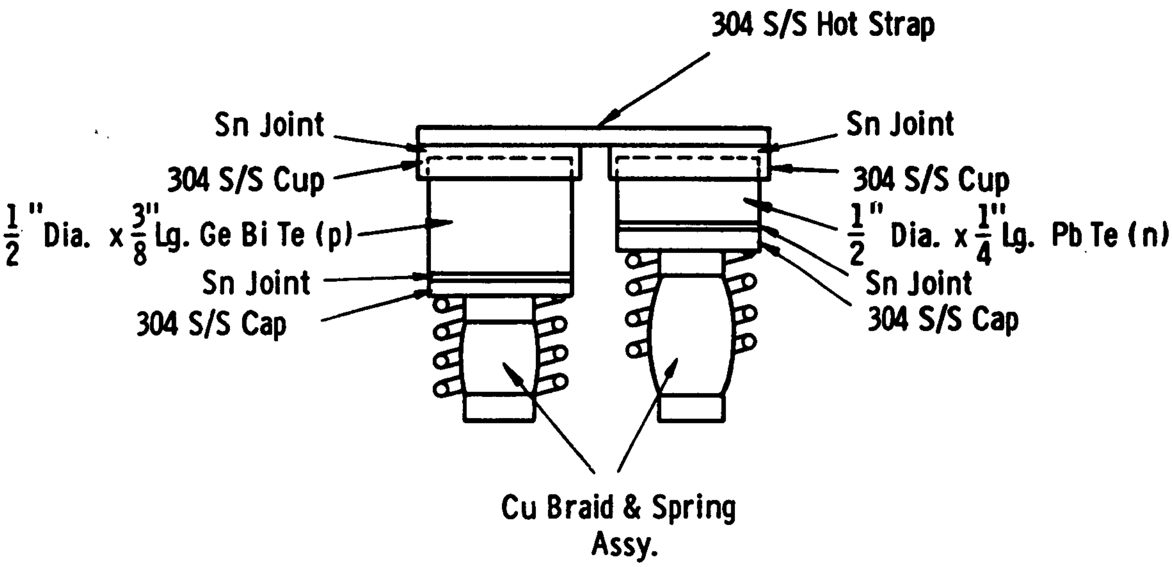


Fig. 3—Pb Te-Ge Bi Te couple with Sn diffusion joints
MIP-III

TABLE I

INITIAL PERFORMANCE OF MODULE SECTIONS

No. Couples	T_H, °C Av. 5 Points	T_c, °C Av. 5 Points	ΔT, °C	I Amps	V_L Volts	V_o Volts	R_i mΩ	P Watts
MIP-I								
24	393	113	280	7.9	1.26	2.55	163	9.99
MIP-II								
10	446	43	403	17.0	0.60	1.20	35.2	10.2
MIP-III								
10	485	66	411	18.0	0.80	1.48	36.1	15.1

APPENDIX A

TESTER FOR GENERATOR THERMOCOUPLES IN CONTROLLED ATMOSPHERE

C. K. Strobel

This appendix describes a tester designed to measure performance and life of a generator thermocouple in a controlled atmosphere. The tester is the calorimeter type consisting of a nine-inch diameter glass bell jar cover over a circular metal base on which the heat sinks with calorimeters and the spring-loaded heat source elevated on vertical adjusting screws are mounted. The arrangement is such that the generator couple can be placed vertically between the heat sinks at the bottom and heat source at the top. Provisions are included for measurement-thermocouples, electric lead wires, water connections and atmosphere-control connections.

Figures 1, 2, and 3 show the general construction of the tester. The performance evaluation is obtained from a comparison of data in tests, using the same couple, in an earlier tester and in the tester described in this appendix. It should be noted here that different methods of measuring couple heat flows were used in the two testers. In the earlier tester which will be referred to as the case loss type A, the couple heat flow was obtained by subtracting the calibrated tester case losses from the measured source heater power. In the present tester, which will be referred to as the sink loss type B, the couple heat flow was obtained by subtracting the calibrated stray heat flow to the sinks from the measured total heat flow to the sinks.

Referring to Figure 1, the tester of the present study consists of the test equipment mounted on a horizontal circular brass plate, which is supported by legs at the bottom and provided with a bell jar cover for the top. The equipment is mounted on the base plate inside of the jar with provisions for atmosphere, water and electrical control from the outside. The overall outside dimensions, exclusive of support legs, are about 9-1/2 in. dia. by 18 in. high and the overall dimensions of the test equipment are about 4-1/4 in. dia. by 6 in. high.

The base plate supports the test equipment and contains sealed connections to the outside for water, gas and electricity. It also has O-ring seals for the bell jar and the sink case which can be oriented for convenience in mounting of the couple. The inlet and outlet water tubes are soldered into the base of the sink casing. The other connections are sealed through the main base with the aid of O-ring flanges. These are the gas or pumping connection, the current leads with the aid of glass insulators, and both the thermocouple and voltage leads with the aid of "Conax" thermocouple glands. The orientation of the tester and the location of the leads in the "Conax" glands shown in the drawings are for clarity and not necessarily the same as used in the testing for this study.

The sink assembly consists of the water cooled sinks with associated reservoirs mounted centrally in a stainless steel container and packed with potassium titanate insulation. The container is a thin-wall cup, about 4-1/4 in. OD by 2-1/4 in. high with a bottom O-ring projection, about 2-1/4 in. OD

by 1/2 in. high. There are two separate heat sinks, electrically and thermally insulated from each other with insulating spacers at top and bottom and supported on a layer of potassium titanate in the bottom of the container, so that the top surfaces of the sinks are level with the top edge of the container. Each sink has a single-layer copper-tube helical cooling coil, the ends of which are connected to reservoirs which have tube extensions through the titanate and container base to inlet and outlet water connections. Each of the two inlet lines is equipped with a separate water flowmeter, (not shown) which is calibrated for calorimeter measuring purposes.

Further details on the calorimeter may be seen by referring to Figures 2 and 3. For each heat sink, there are two cylindrical copper reservoirs, each containing an insulated thermocouple well. One reservoir is connected in the water inlet line and the other in the water outlet line, for each sink cooling coil. The inlet reservoir is thermally isolated from the cooling coil by a rubber tube connection and the outlet reservoir is thermally isolated from the water supply line by a rubber tube connection. For each sink, the two measuring thermocouples (0.010 in. dia. chromel-alumel wires), inserted in the wells of the inlet and outlet reservoirs, are connected electrically in series opposing so as to provide for measurement of the difference between outlet and inlet water temperatures with the aid of a potentiometer. This temperature difference and the water flow-rate are used to calculate the heat flow to the sink. Disturbing heat flows, from the sink to the inlet calorimeter reservoir and from the outlet calori-

meter reservoir to the outlet water tube, are made negligible by use of the rubber tube connections, mentioned earlier. Other calibrated stray heat losses, obtained from measurements with the test couple replaced with titanate insulation, are subtracted from the sink heat flows to obtain the heat flow through the couple.

The heat source assembly is somewhat similar to the sink assembly. A 115V-100W cartridge heater, 1-3/8 in. long by 3/8 in. dia. is mounted in a length wise hole in a rectangular stainless steel block, 2 in. by 3/4 in. by 3/4 in. The block, with thin stainless steel supports, is mounted centrally on the inside bottom of a cup-shaped stainless steel container (3-7/8 in. OD by 1-1/2 in. high), so that the block face (2 in. by 3/4 in.) is level with the circular edge of the container. There are two thermocouples, one for temperature measurements and one for a Magamp temperature control, inserted in lengthwise thermocouple holes in the block. The thermocouples consist of 0.005 in. dia. chromel-alumel wires in an inconel sheath 0.042 in. dia. The thermocouples and heater leads are brought out through holes in the cup container. Potassium titanate insulation, flush with the circular edge of the container, imbeds the source.

The bottom of the container cup is attached to a horizontal triangular stainless steel plate, which has mounting holes with insulating bushings at the corners. The bushings have clearance holes for the three threaded vertical stainless steel rods which are mounted on the bell jar base. The triangular plate is placed on the rods so that the cup is inverted

and the face of the source rests on the hot junction strap of the couple to be tested. Compression springs with adjusting nuts are placed on the rods on top of the plate so that the nuts might be tightened to obtain the desired assembly force on the test couple. (10 pounds per leg for the present tests.)

In general, the couple to be tested is mounted between the source and sinks (with a thermal resistor and ball type of joint interposed between the cold end and sink for each leg), so that mechanical strains are minimized, the heat flow is directed downward through the couple, and there are provisions for temperature and electrical measurements. For the present tests, the arrangement was as shown in Figure 1 except that a thin (0.001 in.) sheet of mica was used between the source and hot junction strap and the thermal resistors were omitted at the cold ends. The mica prevented electrical resistance changes with contact variations and the ball and socket joints, between the cold ends and sinks, prevented serious mechanical strains in the couple. All pressure contact surfaces at the cold ends, including those of the ball and socket joints, were coated with gallium-indium liquid alloy to ensure low resistance through the joints. Split and cored disks of potassium titanate were inserted around the couple, between the source and sink, for heat insulation. Sheathed thermocouples and stainless steel wire voltage leads, attached in holes in the back strap and cold end terminal disks, were used with appropriate meters for temperature and voltage measurements. Electric current measurements were made with the aid of a 50 mv-50 amp shunt, a variable resistance and a switching device, connected in series with the sink cooling coils as shown in Figures

2 and 3. In this circuit the test thermocouple was the electric generator; the sinks with cooling coils were the generator terminals; and the shunt with variable resistor was the load.

The unencapsulated thermocouple, No. 93, used for the tests of this study, consisted basically of a parallel mounting of a P-leg and an N-leg on a common stainless steel back strap with stainless steel flat disks, 3/32 in. thick, attached to the free ends. The semiconductor material in each leg was about 1/4 in. long by 1/2 in. dia; germanium bismuth telluride, batch No. GBT 93-3-15, for the P-leg; lead telluride batch No. Q-24 for the N-leg. The leg contact faces for use at the cold junction were initially flat and those for use at the hot junctions were initially 0.001 in. deep concave. The back strap, 1-3/8 in. by 3/4 in. by 1/4 in., had two flat-bottom circular recesses, 0.505 in. dia. by 0.064 in. deep, into which the hot junction ends of the legs were inserted. Before assembly, the contact faces of the stainless steel parts and the ends of the legs were coated with a tin solder which was then diffused by a heat treatment. The parts were then tin-soldered together without further diffusion treatment.

Couple No. 93 was tested first at room ambient in the case loss type of tester. Basically, the couple with electric leads and measuring thermocouples attached, was mounted in a vertical cylindrical case between an electric heat source at the bottom and water-cooled spring-loaded heat sinks at the top, so that there was a force of about 10 pounds on each leg. A sheet of 0.001 in. mica was placed between the heat source and hot junction strap, and a gallium-indium layer was used between the cold ends and sinks. The casing was filled

with potassium titanate insulation and had measuring thermocouples attached to the outside for use in determining the average case temperatures. The average case temperatures were used to determine the test couple heat flow by correcting the electric heater power for case losses, obtained from a calibration of average case temperature versus heater power with potassium titanate insulation substitution for the test couple.

Steady-state electrical and temperature measurements were made, with appropriate meters, at the start and at intervals during 37 days of matched load life test. For these measurements, the source temperature was adjusted for 450°C at the hot junction, with the sinks water-cooled by a constant water flow, and the couple on open circuit. After the open circuit measurements, matched load was applied without changing the source temperature control, and the closed circuit measurements were made. Then the test was continued with matched load. In addition, on the last day of test, a third set of data was obtained with matched load and the source temperature raised so as to elevate the hot junction temperature to 450°C. The measurements made on the last day of the life test, along with the calculated couple properties, are recorded in Tables I and II of this appendix.

After the above test, couple No. 93 was transferred to the sink loss type of tester for performance measurements both at room atmosphere conditions and in argon atmosphere at about 12 psi. For these tests, the couple was mounted in the tester as described earlier with reference to Figure I, except the bell jar cover was not used in the case of the room atmosphere test.

For the test in argon, the bell jar enclosure was evacuated at a pressure of less than 5 microns for 24 hours (to remove moisture from the titanate insulation) and then back filled with argon to a pressure of about 12 psi.

Steady state open and closed circuit couple measurements were made in the same manner as with the case loss type of tester. With both testers, steady state condition was obtained after operation for about an hour at a given setting.

Data for calculating the total and stray heat flows to the sinks were obtained by calibration tests. For the case of total heat flow each flowmeter in the sink water supplies was calibrated by measuring the amount of water which flowed in two minutes for a scale reading of 16 divisions. Since it was fouud that the flows might vary as much as from 34 to 26 cu cm per minute (cu cm and ml considered same), because of contamination of the flowmeters with prolonged usage, the flowmeters were calibrated for each test. For the case of the stray heat flows, for each of the two ambient conditions, measurements were made of the total heat flow to the sinks for various source temperatures, when the test couple was replaced with the same form of potassium titanate insulation. The calculated heat flow through the titanate, replacing the couple, was subtracted from the measured total heat flow to obtain the correction for stray heat flow. The correction factors were 3.30 watts for a source temperature of about 500°C in the case of the room atmosphere ambient and 2.8 watts at a source temperature of about 510°C in the case of the argon ambient.

The test data and calculated performance characteristics obtained with couple No. 93 in the sink loss type of tester are recorded in Tables I and II. In order to illustrate an advantage of this type of tester, in providing for heat flow measurements in each leg separately, performance characteristics for each leg in the argon ambient test, are also shown in Table II. It should be noted that the individual leg data are not for the equivalent of matched load for each leg.

Referring to the earlier descriptions of the testers and to the three lines of data listed in Table I, for the room atmosphere ambient conditions, for both testers A and B, it will be seen that the test conditions for the couple in the two testers were generally comparable. The basic difference was that the ball and socket joints at the cold ends of the couple in tester B caused the temperature drop across the couple in this tester to be a little lower than the drop obtained in tester A without the ball and socket joints. This lower drop with practically the same hot junction temperatures caused the average temperature of the couple to be higher in tester B than in tester A. These differences in temperature conditions can partly account for the slight differences observed in comparing the other data for the testers in the lines referred to above, as will become apparent from the following discussion of the associated data in Table II.

In Table II, a comparison of the room-ambient couple performance data, listed in the three lines for tester B with the corresponding data for tester A, shows that generally the data obtained with the two different

types of testers are in close agreement and that the lack of agreement is consistent with the difference in couple temperatures. The lower Seebeck coefficient for the couple at the higher average temperature in tester B is consistent with the saturation at the higher temperatures shown for the Seebeck coefficient versus temperature curves which we have available for thermoelectric materials similar to those used here. Also assuming a positive temperature coefficient of resistance for the thermoelectric materials, we might expect the higher resistance values at the higher average temperatures in tester B as shown by the data. In the case of thermal conductivities, the temperature coefficients might be either slightly positive or negative, and the values obtained should agree closely as shown in the table. The lower temperature drop across the couple in tester B, should cause both the lower value of heat flow and the lower value of efficiency (lower Carnot value) shown in Table II for tester B. Thus, considering that we might expect some differences caused by transferring the couple from one tester to the other, the data obtained with the same couple in the two testers are in good agreement.

The vertification of the agreement of the test results with the two testers was the major purpose of this investigation. The agreement shows that either tester might be used for couple measurements involving heat flows and efficiencies at room ambient and that the efficiencies have been verified by two different methods of test. Also the values of resistances and Seebeck coefficients obtained with these testers are in close agreement with values measured for single legs of similar materials

in other test devices at our laboratory.

The other data in Table I and II are supplementary but present additional information which is of importance in our testing. The data in the third line, under the room atmosphere tests for both testers in both tables, show that there is no great error introduced by not raising the hot junction temperature back to its initial value after the load is connected to the couple. These data also show the magnitude of the errors involved. The tests with different atmospheres in tester B show that initially the data for the complete couple are essentially the same in room air or argon.

The calculated performance for the P-leg and N-leg separately, as tabulated in Table II, illustrates the additional feature of tester B which provides for obtaining values of thermal conductivity and efficiency of the leg materials separately. There will be some errors introduced by contact and strap resistance but these should not be large for a newly made couple. Also, if desired, the couple loading could be adjusted to obtain the equivalent of matched load for each leg separately.

Unfortunately, we cannot compare the values obtained in the present tests with literature values since we do not have the specifications or reference data for the materials used for couple 93, and the data recorded are values obtained after 37 days of life test. However, the initial Seebeck coefficient and electrical resistivity values (obtained in tester A) of 148 microvolts per °C and 1.51 milliohm cm respectively for the P-leg, and 196 microvolts per °C and 2.72 milliohm cm respectively for

the N-leg, are consistent with corresponding literature values for similar materials at an average temperature of about 520°K. Also the initial value of 0.02 watts per cm per °C for each leg, estimated from the values in Table II and the amount of change in combined thermal conductivity in 37 days of test, is consistent with literature values for similar materials. These values indicate that fairly accurate results should be expected from measurements of thermoelectric properties with such testers.

Acknowledgements

I wish to acknowledge the assistance of H. R. Ryden and W. R. Miller in the design, of W. R. Miller in the apparatus set-up and of C. A. Dirkmaat in the measurements.

Table I

Experimental Data for Operating Characteristics of Couple No. 93. Obtained with Case Loss Type of Tester (A) and with Sink Loss Type of Tester (B). Hot Junction-About 450°C. Cold Junctions-Water-Cooled.

Source Temp. °C	Couple Temperatures °C Hot End T_H	Cold Ends - Tc P-Leg	N-leg	Avg.	Avg. Diff.	Avg. Case Temp. °C	Calorimeter* Temp.Diff. °C P-leg	N-leg	Voltages - mv Total Couple	P leg	N Leg	Output Current Amps.	Input Power Watts
In Tester A with Room Atmosphere. At the End of 37 Days of Life Test in A.													
a	450.0	33.7	34.5	34.1	415.9	57.3	-	-	154.4	68.1	84.5	0	44.0
b	442.2	35.9	36.9	36.4	405.8	57.3	-	-	77.2	39.3	36.8	24.22	49.0
c	450.0	36.1	37.1	36.6	413.4	58.9	-	-	77.2	39.5	36.2	24.92	49.8
In Tester B with Room Atmosphere. After 37 Days of Life Test in A.													
496.3	450.6	49.6	40.0	44.8	405.8	-	7.53	7.70	144.0	64.0	78.8	0	-
496.3	444.8	52.9	42.3	47.6	397.2	-	8.23	8.53	72.0	35.5	35.3	22.20	-
501.8	450.4	53.3	42.7	48.0	402.4	-	8.43	8.68	72.0	35.7	35.2	22.66	-
*Flow rate in each calorimeter = 29.6 cu cm/min													
In Tester B with Argon Atmosphere. After Above Test.													
507.8	450.2	47.9	37.9	42.9	407.3	-	7.68	7.68	144.6	64.2	79.9	0	-
507.0	441.8	50.8	41.0	45.9	395.9	-	8.33	8.38	72.3	35.6	36.4	21.80	-
515.8	450.0	52.5	42.6	47.5	402.5	-	8.70	8.80	72.3	35.7	35.8	22.41	-

* Flow rate in each calorimeter = 28.9 cu cm/min.

a. Source temp. control set for 450°C hot junction with open-circuit couple.

b. Source temp. control unchanged when matched load connected to couple.

c. Source temp. control set for 450°C hot junction with matched load on couple

Table II

Performance of Couple No. 93, Determined from Data Obtained in Tester A and then in Tester B, Under Comparable Operating Conditions. See Table I

T_H T_c °C	Seebeck Micro. V / °C	Voltage Output Millivolts	Match. Couple Amps.	Res. Milliohms Total Couple	Res. Milliohms P Leg	Res. Milliohms N Leg	Correc'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm.	Thermal* Watts / °C	Thermal* Watts / °C cm.
In Tester A with Room Atmosphere. At the End of 37 Days of Life Test in A.												
				For Complete Couple								
415.9	371.5	154.4	0	-	-	-	29.6	0	-	-	0.0711	0.0183
405.8	-	77.2	24.22	3.185	1.188	1.970	35.4	1.870	5.28	3.098	-	-
413.4	-	77.2	24.92	3.099	1.148	1.935	34.9	1.924	5.52	3.010	-	-
In Tester B with Room Atmosphere. After 37 Days of Life Test in A.												
				For Complete Couple								
405.8	354.5	144.0	0	-	-	-	28.1	0	-	-	0.0692	0.0179
397.2	-	72.0	22.20	3.245	1.283	1.960	31.3	1.585	5.06	3.150	-	-
402.4	-	72.0	22.60	3.180	1.249	1.930	31.7	1.632	5.15	3.088	-	-
In Tester B with Argon Atmosphere. After Above Test.												
				For Complete Couple								
407.3	354.7	144.6	0	-	-	-	28.11	0	-	-	0.0689	0.0178
395.9	-	72.3	21.80	3.315	1.312	1.995	30.90	1.577	5.10	3.220	-	-
402.5	-	72.3	22.41	3.225	1.251	1.967	32.40	1.622	5.01	3.132	-	-

Table II (continued)

T_H T_c °C	Seebeck Micro. V °C	Voltage Output Millivolts	Match. Couple Amps.	Res. Milliohms			Correc'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm.	Thermal*	
				Total Couple	P leg	N leg					Watts/°C	Watts/°C
For P-Leg Alone												
402.3	159.9	64.2	0	-	-	-	14.09	0	-	-	0.0350	0.0180
391.0	-	35.6	21.80	-	1.312	-	15.38	0.775	5.05	2.547	-	-
397.5	-	35.7	22.41	-	1.251	-	16.11	0.800	4.96	2.432	-	-
For N-Leg Alone												
412.3	193.8	79.9	0	-	-	-	14.09	0	-	-	0.0342	0.0176
400.8	-	36.4	21.80	-	-	1.995	15.49	0.794	5.13	3.882	-	-
407.4	-	35.8	22.41	-	-	1.967	16.35	0.801	4.90	3.820	-	-

* Combined values for case of complete couple.

Sample Calculations - Tester B - Argon Atmosphere - Source Temperature not Adjusted for Electrical Load

For Complete Couple

$T_H - T_c = 450.2°C - 42.9°C = 407.3°C$ (open couple circuit)

$T_H - T_c = 441.8°C - 45.9°C = 395.9°C$ (load couple circuit)

$$\text{Seebeck Coefficient} = \frac{\text{open couple microvolts}}{T_H - T_c} = \frac{144.6 \text{ mv}}{407.3 \text{ °C}} = 354.7 \frac{\text{microvolts}}{\text{°C}}$$

$$\text{Corrected Heat Watts (open circuit)} = \frac{\text{vol. of water}}{\text{sec}} \times \text{density water}$$

$$\times \text{ Temp. Rise} \times \text{specific heat} \times \frac{4.19 \text{ watt sec}}{\text{calorie}} - \text{stray heat flow}$$

$$= \frac{28.9 \text{ cu cm}}{\text{min}} \times \frac{1 \text{ min.}}{60 \text{ sec}} \times \frac{1 \text{ g}}{\text{cu cm}} \times (7.68 + 7.68)\text{°C} \times \frac{1 \text{ calorie}}{1 \text{ g} \times 1\text{°C}}$$

$$\times \frac{4.19 \text{ watt sec}}{\text{calorie}} - 2.80 \text{ watts} = 30.91 \text{ watts} - 2.80 \text{ watts} = 28.11 \text{ watts}$$

Thermal watts per °C through both legs = corrected heat watts per °C

$$= \frac{28.11 \text{ watts}}{T_H T_c \text{ (open)}} = \frac{28.11 \text{ watts}}{407.3\text{°C}} = 0.0689 \frac{\text{watts}}{\text{°C}}$$

Equivalent thermal conductivity at two legs of thermoelectric material in parallel = k = combined thermal watts $\times \frac{\text{length one leg}}{\text{2x area one leg}}$.

Measured length of each leg = 0.653 cm = ℓ

$$\text{Area of each leg} = \frac{3.14 \times (1.27 \text{ cm})^2}{4} = 1.265 \text{ sq. cm.} = A$$

$$\frac{\ell}{A} = \frac{0.653 \text{ cm.}}{1.265 \text{ sq. cm.}} = \frac{0.515}{\text{cm}} \qquad \frac{A}{\ell} = 1.942 \text{ cm.}$$

$$k = \frac{0.0689 \text{ watts}}{\text{°C}} \times \frac{0.515}{2 \text{ cm}} = 0.0178 \frac{\text{watts}}{\text{°C cm.}}$$

Corrected heat watts for closed circuit with matched load

$$= \frac{28.9 \text{ cu cm}}{\text{min.}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ g}}{\text{cu cm}} \times (8.33 + 8.38)\,^\circ\text{C} \times \frac{1 \text{ cal.}}{1\text{g} \times 1\,^\circ\text{C}}$$

$$\times \frac{4.19 \text{ w sec}}{\text{cal.}} - 2.80\text{W} = 33.70\text{W} - 2.80\text{W} = 30.80 \text{ watts}$$

Electric power output at matched load = load (volts x amps)

$$= 72.3 \times 10^{-3}\text{v} \times 21.80 \text{ amp.} = 1.577 \text{ watts}$$

$$\text{Efficiency} = \frac{\text{elec. output}}{\text{heat input}} \times 100 = \frac{1.577\text{w}}{30.90\text{w}} \times 100 = 5.10 \text{ percent}$$

$$\text{Couple resistance} = \frac{\text{internal voltage drop with load}}{\text{load amps.}} = \frac{144.6 \text{ mv} - 72.3 \text{ mv}}{21.8 \text{ amp.}}$$

$$= 3.315 \text{ milliohms}$$

Equivalent electrical resistivity of two legs in series = couple resistance

$$\times \frac{A}{2} = 3.315 \text{ milliohm} \times 0.971 \text{ cm} = 3.220 \text{ milliohm cm.}$$

For P-Leg Alone

$T_H - T_c$ (open) = 450.2°C - 47.9°C = 402.3°C

$T_H - T_c$ (closed) = 441.8°C - 50.8°C = 391.0°C

$$\text{Seebeck coefficient} = \frac{64.2 \text{ mv}}{402.3\,^\circ\text{C}} = 159.9 \frac{\text{microvolts}}{^\circ\text{C}}$$

$$\text{Corrected heat watts (open)} = \frac{28.9 \text{ cu cm}}{\text{min.}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1\text{g}}{\text{cu cm}} \times 7.68\,^\circ\text{C} \times \frac{1 \text{ cal.}}{1\text{g } 1\,^\circ\text{C}}$$

$$\times \frac{4.19 \text{ watt sec}}{\text{cal.}} - 1.40\text{W} = 15.49\text{W} - 1.40\text{W} = 14.09\text{W}$$

$$\frac{\text{Thermal watts}}{°\text{C}} = \frac{14.09\text{W}}{402.3°\text{C}} = 0.0350 \frac{\text{W}}{°\text{C}} .$$

$$\text{Thermal conductivity} = 0.0350 \frac{\text{W}}{°\text{C}} \times \frac{0.515}{\text{cm}} = 0.0180 \frac{\text{W}}{°\text{C cm}}$$

$$\text{Corrected heat watts (closed)} = \frac{28.9 \text{ cu cm}}{\text{min.}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1\text{g}}{\text{cu cm}} \times 8.33°\text{C}$$

$$\times \frac{1 \text{ cal.}}{1\text{g} \times 1°\text{C}} \times \frac{4.19 \text{ w sec}}{\text{cal.}} - 1.4\text{W} = 16.78\text{W} - 1.4\text{W} = 15.38\text{W}.$$

Electric power output = 35.6 mv x 21.8 amp = 0.775W.

$$\text{Efficiency} = \frac{0.775\text{W}}{15.38\text{W}} \times 100 = 5.05 \text{ percent.}$$ (Not for matched load).

$$\text{Resistance} = \frac{64.2 \text{ mv} - 35.6 \text{ mv}}{21.8 \text{ amps}} = \frac{28.6 \text{ mv}}{21.8 \text{ amp}} = 1.312 \text{ milliohms.}$$

Resistivity = 1.312 ohms x 1.942 cm = 2.547 milliohm cm.

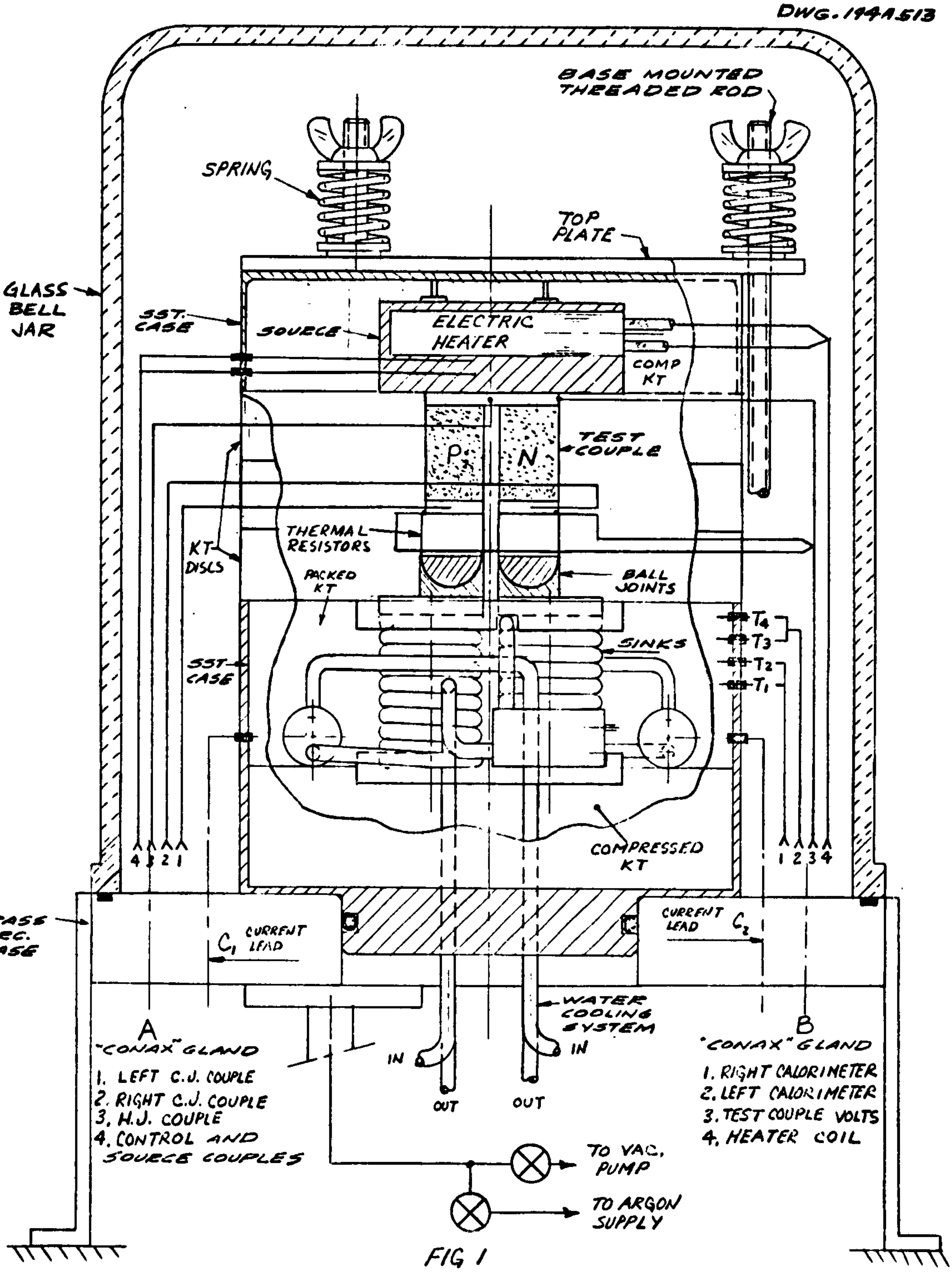
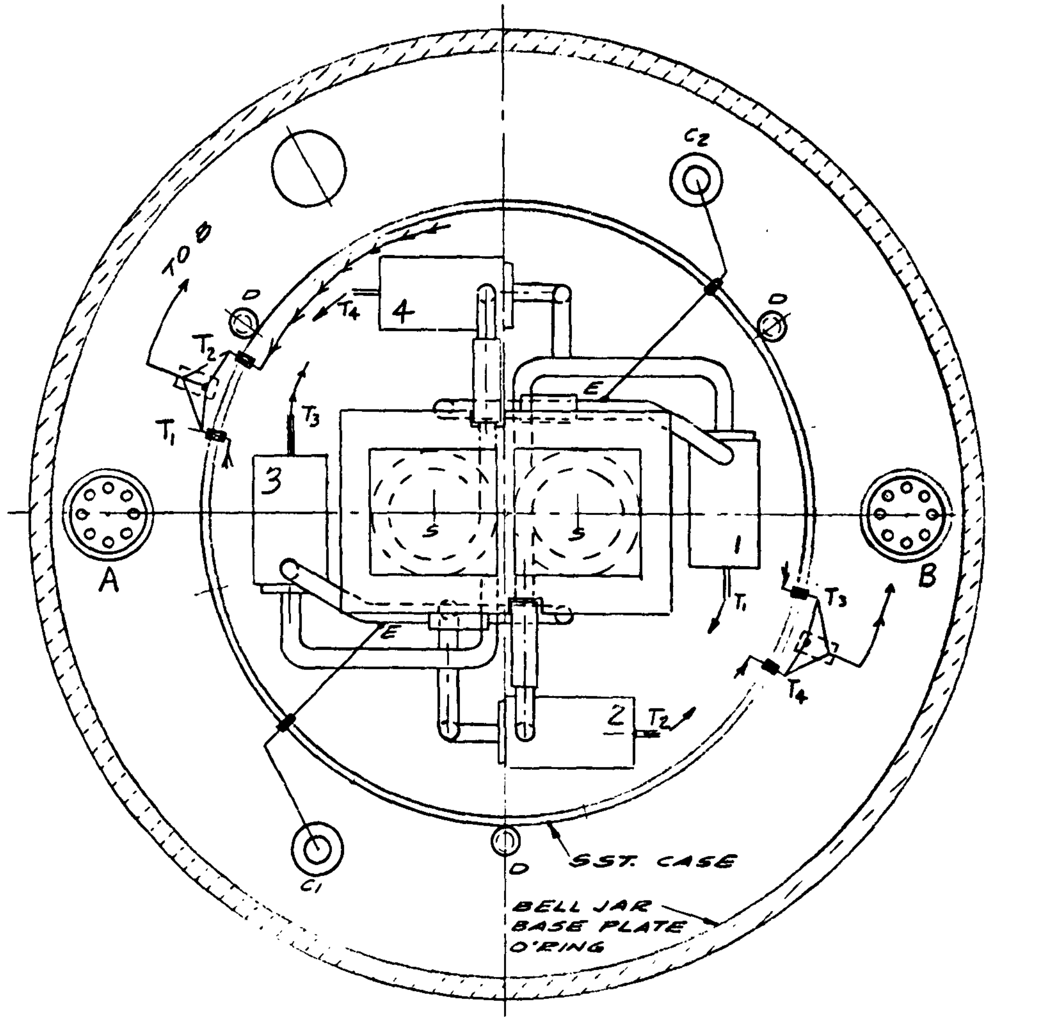


FIG 1

SIDE VIEW OF CONTROLLED ATMOSPHERE THERMOCOUPLE TESTER

DWG. 194A514



S - SINKS
1,2,3,4 - CALORIMETER RESERVOIRS
T - THERMOCOUPLES
C_1, C_2 - SEALED CURRENT LEAD TERMINALS
A,B - "CONAX" GLANDS
D - THREADED ROD HOLES
E - CURRENT LEADS SOLDERED

FIG. 2
TOP VIEW OF HEAT SINKS AND CALORIMETERS OF CONTROLLED ATMOSPHERE THERMOCOUPLE TESTER.

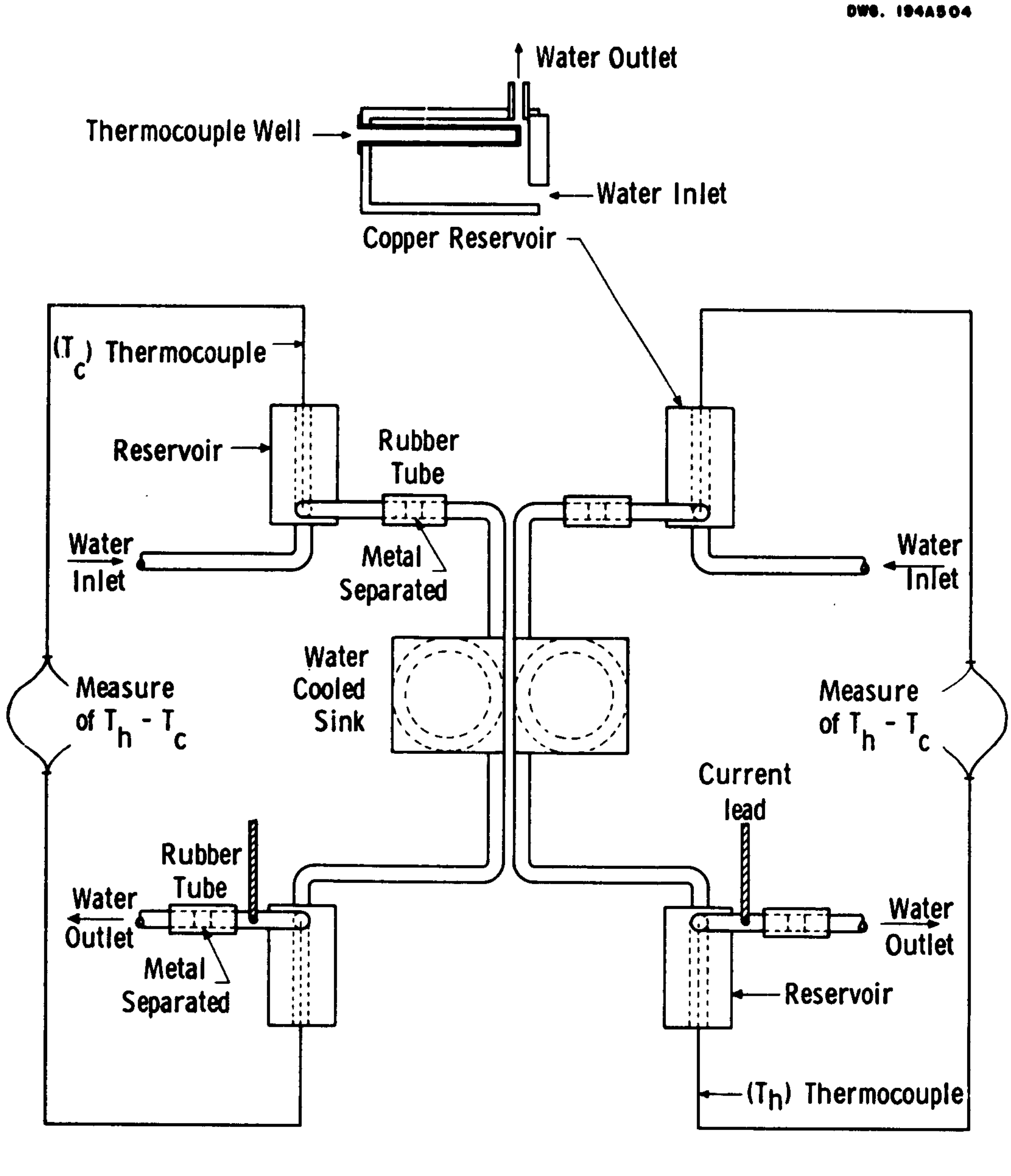


Fig. 3--Schematic arrangement of heat sinks and calorimeters of couple tester

APPENDIX B

PERFORMANCE OF ZINC ANTIMONIDE, GERMANIUM BISMUTH TELLURIDE AND LEAD TELLURIDE IN GENERATOR THERMOCOUPLE ASSEMBLIES

C. K. Strobel

The results of some recent tests are being reported here in order to accumulate both performance data on the materials which are presently being considered for semiconductor thermocouple generators, and reliability data on a new tester. The tests were made with two similar unencapsulated thermocouples, Nos. 107 and 115B, under comparable conditions, in the controlled atmosphere couple tester B described in Appendix A.

Each of the two couples consisted basically of a parallel mounting of a P-leg and an N-leg on a common flat steel back-strap, 1-3/8 in. by 3/4 in. by 1/4 in. The strap was low carbon steel for couple No. 107 and stainless steel for couple No. 115B. A flat stainless steel disk, 1/2 in. diameter by 3/32 in. thick, was attached to the free end of each leg. The dimensions of three of the legs were 1/2 in. diameter by 1/2 in. long and of the fourth leg (zinc antimonide) were 1/2 in. diameter by 15/32 in. long. Couple No. 107 was made with a zinc antimonide P-leg (batch HT 3072) and a lead telluride N-leg (batch HT 3249). Couple No. 115B was made with a germanium bismuth telluride P-leg (batch B-36) and a lead telluride N-leg (batch HT 3249. Both N-legs were made from the same batch of material. The ends of all legs were initially flat. Before assembly, the contact faces

of all steel parts and the ends of the legs were coated with a tin solder which was then diffused by a heat treatment. The parts were then tin-soldered together without further diffusion treatment. Appropriate holes in the end disks and back-straps provided for the attachment of measuring thermocouples and stainless steel voltage measurement leads. It should be pointed out that these couples were designed for initial testing only and not for long life with heat cycling.

For testing, each generator couple in turn was mounted between the heat source at the top and two separately cooled heat sinks at the bottom in such a way as to obtain a compressive force of 10 pounds on each leg. A thin (0.001 in.) sheet of mica was interposed between the source and hot junction strap to prevent electrical resistance changes with contact variations. A ball and socket joint was interposed between the cold ends and sink for each leg in order to minimize mechanical strains in the couple. All pressure contact surfaces at the cold ends, including those of the ball and socket joints, were coated with gallium-indium liquid alloy to ensure low electrical and thermal resistance through the joints. Split and cored disks of potassium titanate were inserted around the couple, between the source and sinks, for heat insulation.

The tests were conducted in an argon atmosphere at about 12 psi. With the source temperature and calorimeter water flows held constant for a given test, measurements were made of the source temperatures, couple junction temperatures, couple voltages, couple current, calorimeter temperatures and

calorimeter water flows. From these measurements the characteristics of the complete couple and of each leg separately were determined.

Three different tests were conducted with each of the two generator thermocouples (Nos. 107 and 115B) under steady state operating conditions. Each of these tests was the same for each couple. In the first test, the hot junction strap was at a temperature of 450°C, the cold end sinks were water cooled and the output circuit of the couple was open. For the second test, the couple circuit was closed through a matched load without changing the control temperature of the heat source. The third test was similar to the second test except that the source temperature control was adjusted to raise the hot junction strap temperature back to 450°C with matched couple load. The water flows to each of the two sinks and calorimeters were held at the same constant values for all six tests. The experimental and performance data for these couples are recorded in Tables I and II.

From Table I, it may be seen that the test conditions for the two generator couples were comparable in each of the three tests. Small differences in temperature drops across the couples probably resulted from differences in thermal conductivities and Peltier effects.

The data of Table II show not only the consistency of the measured material characteristics with literature values but also the compatibility of the thermoelectric materials with assembly materials. The calculated values of Seebeck coefficient, electrical resistivity, and thermal conductivity for each of the three materials at an average operating temperature of about 515°K are

consistent with literature values which we have available for similar materials. In the assemblies, the pure tin solder seemed to be satisfactory for all junctions. Lead telluride gave equally good performance when assembled either on a low carbon steel or a stainless steel hot junction strap. For the P-legs, zinc antimonide on a low carbon steel strap and germanium bismuth telluride on a stainless steel strap were about equal in regard to electric power output and overall efficiency. The values of output voltage and internal resistance were lower for the zinc antimonide than for the germanium bismuth telluride. Since lead telluride gave equally good performance on either strap material, it might be assumed that a stainless steel back-strap would be satisfactory for zinc antimonide although this has not been tried experimentally. It appears that either couple might be considered for operation, in the temperature range used here, provided known assembly methods are used to provide for life with heat cycling. There is some preference for couple No. 115B in that all of its materials are operable at temperatures appreciably above 450°C whereas couple No. 107 is limited to about 450°C operation by the zinc antimonide and to some extent by the low carbon steel.

Table I

EXPERIMENTAL DATA FOR OPERATING CHARACTERISTICS OF COUPLES NOS. 107 AND 115B IN ARGON TESTER B

Source Temp. °C	Couple Temperatures °C					Calorimeter Temp. Diff. °C		Voltages - mv			Output Current Amps
	Hot End T_H	Cold Ends - Tc			Avg. Diff.						
		P-leg	N-Leg	Avg.		P-leg	N-leg	Total Couple	P Leg	N Leg	
Couple No. 107 (steel strap, zinc antimonide P-leg, lead telluride N-leg)											
483.8	450.6	34.0	29.3	31.6	419.0	4.03	3.53	172.4	82.2	89.5	0
482.8	443.5	37.2	32.6	34.9	408.6	4.53	4.03	86.2	40.0	45.5	15.27
489.0	450.0	36.5	31.9	34.2	415.8	4.58	4.25	86.2	40.0	45.3	15.66
Couple No. 115B (stainless steel strap, germanium bismuth telluride P-leg, lead telluride N-leg)											
484.6	450.4	36.2	29.5	32.8	417.6	3.83	3.58	150.6	62.1	87.2	0
484.2	443.5	38.1	31.6	34.8	408.7	4.45	4.48	75.3	34.6	39.8	18.11
491.0	450.0	39.0	32.5	35.7	414.3	4.53	4.45	75.3	35.0	39.7	18.36

Table II

PERFORMANCE OF COUPLES NOS. 107 and 115B, UNDER COMPARABLE OPERATING CONDITIONS, IN TESTER B. (See Table I)

T_H T_c °C	Seebeck Micro. V/°C	Voltage Output Millivolt	Match Couple Amps.	Res. Milliohms Total Couple	Res. Milliohms P Leg	Res. Milliohms N Leg	Correc'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm.	Thermal* Watts/°C	Thermal* Watts/°C cm.
For Complete Couple No. 107 (legs on low carbon steel strap)												
419.0	411.5	172.4	0	-	-	-	14.8	0	-	-	0.0354	0.0171
408.6	-	86.2	15.27	5.649	2.765	2.880	16.9	1.318	7.81	2.896	-	-
415.8	-	86.2	15.66	5.510	2.700	2.825	17.3	1.348	7.79	2.835	-	-
For P-leg Alone (zinc antimonide)												
416.7	197.2	82.2	0	-	-	-	8.08	0	-	-	0.0194	0.0182
406.3	-	40.0	15.27	-	2.765	-	9.13	0.610	6.69	2.940	-	-
413.5	-	40.0	15.66	-	2.700	-	9.08	0.626	6.89	2.867	-	-
For N-leg Alone (lead telluride)												
421.3	212.2	89.5	0	-	-	-	6.76	0	-	-	0.0161	0.0161
410.9	-	45.5	15.27	-	-	2.880	7.85	0.694	8.84	2.870	-	-
418.1	-	45.3	15.66	-	-	2.825	8.22	0.709	8.64	2.817	-	-
For Complete Couple No. 115B (legs on stainless steel strap)												
417.6	360.2	150.6	0	-	-	-	14.39	0	-	-	0.0344	0.0172
408.7	-	75.3	18.11	4.16	1.517	2.615	17.35	1.363	7.85	2.072	-	-
414.3	-	75.3	18.36	4.11	1.475	2.588	17.35	1.382	7.96	2.048	-	-
For P-leg Alone (germanium bismuth telluride)												
414.2	150.1	62.1	0	-	-	-	7.58	0	-	-	0.0183	0.0184
405.4	-	34.6	18.11	-	1.517	-	8.78	0.626	7.14	1.512	-	-
411.1	-	35.0	18.36	-	1.475	-	8.89	0.642	7.23	1.471	-	-

Table II (continued)

T_H T_c °C	Seebeck Micro. V / °C	Voltage Output Millivolt	Match Couple Amps	Res. Milliohms Total Couple	P Leg	N Leg	Correc'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm.	Thermal * Watts / °C	Watts / °C cm.
For N-leg Alone (lead telluride)												
421.0	207.2	87.2	0	-	-	-	6.80	0	-	-	0.0162	0.0162
412.0	-	39.8	18.11	-	-	2.615	8.56	0.721	8.42	2.608	-	-
417.6	-	39.7	18.36	-	-	2.588	8.42	0.729	8.65	2.479	-	-

* Combined values for case of couples

APPENDIX C

EFFECT ON INITIAL PERFORMANCE OF RECESSING THE HOT JUNCTION STRAP OF A GERMANIUM BISMUTH TELLURIDE - LEAD TELLURIDE GENERATOR THERMOCOUPLE

C. K. Strobel

In the continued development of semiconductor thermocouples for generators, data have been obtained with two generator couples on the effect on initial performance of one of the known assembly modifications for improvement of heat cycling life. The description and initial performance of the first couple, No. 115B, which was designed with flat pellet ends on a plain flat hot junction strap for initial testing only, are covered in Appendix B. The description and initial performance of a second similar couple, No. 118, having a recessed hot junction strap to improve heat cycling life, are covered in this appendix. Heat cycling life test data, showing beneficial effects of recessing, have been obtained in laboratory tests but are not included here. This discussion deals only with a comparison of the initial performance qualities of the two couples mentioned above, to show any effects of recessing.

Each of the unencapsulated couples, Nos. 115B and 118, used for the tests of this study, consisted basically of a parallel mounting of a P-leg and an N-leg on a common stainless steel hot junction strap, 1-3/8 in. by 3/4 in. by 1/4 in., with a stainless steel flat disk, 1/2 in. diameter by 3/32 in. thick, attached to the free end of each leg. The semiconductor material in each leg was 1/2 in. diameter by 1/2 in. long; germanium bismuth

telluride, batch No. B-36, for the P-leg; lead telluride, batch No. HT 3249, for the N-leg. The leg contact faces for both hot and cold junctions were initially flat. The hot junction strap was plain and flat for couple No. 115B. For couple No. 118, the strap was similar except for two flat-bottom circular recesses, 0.505 in. diameter by 0.125 in. deep, into which the hot junction ends of the legs were inserted. Before assembly, the contact faces of the stainless steel parts and the legs were coated with a tin solder which was then diffused by heat treatment. The parts were then tin-soldered together without further diffusion treatment. Appropriate holes in the cold junction disks and hot junction strap of each couple were used for attaching voltage leads and instrument thermocouples.

The performance data on the two generator couples were obtained with the controlled atmosphere tester B, which is described in detail in Appendix A. In testing, each couple in turn, in an argon atmosphere at 12 psi, was held between an electrically heated source at the top and two calorimeter heat sinks, one for each leg, at the bottom, so as to obtain a compression force of 10 pounds on each leg. A thin (0.001 in.) sheet of mica was interposed between the source and the hot junction strap to prevent electrical resistance changes with contact variations. A ball and socket joint, coated with liquid gallium indium alloy, was interposed between the cold end of each leg and its heat sink to prevent serious mechanical strains in the couple. From measurements of the various couple temperatures, voltages and currents along with the measurements of the calorimeter temperatures and water flows, the performance

characteristics of each couple were obtained. The couple heat flows were obtained by correcting the measured sink heat flows for the calibrated stray heat flows to the sinks.

Three different tests were conducted with each of the two generator couples under steady-state operating conditions. Each of these tests was the same for each couple. In the first test, the hot junction strap was at a temperature of 450°C, the cold end sinks were water cooled, and the output circuit of the couple was open. For the second test, the couple circuit was closed through a matched load without changing the control temperature of the heat source. The third test was similar to the second test except that the source temperature control was adjusted to raise the hot junction strap temperature back to 450°C with matched couple load. The water flows to each of the two sinks and calorimeters were held at the same constant values for all six tests. The experimental and performance data for these two couples are recorded in Table I and II.

From Table I it may be seen that the test conditions for the two generator couples were comparable in each of the three tests. Small differences in temperature drops across the couples probably resulted from differences in contact resistances, thermal conductivities, and Peltier effects.

The data of Table II show that recessing, as might be expected, had little or no effect on the Seebeck coefficient but did affect the other properties as a result of a shortening of the effective pellet length. Effects of the reduced length were to reduce the resistance and increase the thermal conductance. The lower resistance with unchanged voltage was beneficial in increasing the electric

current output. The higher thermal conductance with unchanged temperature was detrimental in increasing the couple heat flow.

The beneficial effects did not quite outweigh the detrimental effects as evidenced by the generally lower efficiencies for the recessed couple. Although the efficiencies were lower, there was some increase in electric power output with the increased heat flux. This could result in some saving in couple weight when the source heat is plentiful, or an excess generator weight when the source is integral and limited. However the performance measured here, which might have been affected to some extent by ordinary assembly variations, is probably small enough to be neglected for many applications.

The investigation, covered by this memo, was conducted in cooperation with Messrs. C. S. Duncan, S. J. Scuro, and C. A. Dirkmaat, as a part of the general development of thermocouples for generator applications.

Table I

EXPERIMENTAL DATA FOR OPERATING CHARACTERISTICS OF COUPLES NOS. 115B AND 118 IN ARGON IN TESTER B

(germanium bismuth telluride P-leg, lead telluride N-leg, different back straps)

Source Temp. °C	Couple Temperatures °C					Calorimeter Temp. Diff. °C		Voltages - mv			Output Current Amps
	Hot End T_H	Cold Ends - Tc			Avg. Diff.						
		P-leg	N-leg	Avg.		P-leg	N-leg	Total Couple	P Leg	N Leg	
Couple No. 115B (plain stainless steel strap)											
484.6	450.4	36.2	29.5	32.8	417.6	3.83	3.58	150.6	62.1	87.2	0
484.2	443.5	38.1	31.6	34.8	408.7	4.45	4.48	75.3	34.6	39.8	18.11
491.0	450.0	39.0	32.5	35.7	414.3	4.53	4.45	75.3	35.0	39.7	18.36
Couple No. 118 (recessed stainless steel strap)											
480.4	450.0	41.1	30.5	35.8	414.2	4.68	4.45	150.0	63.3	85.8	0
480.4	443.5	43.5	32.2	37.8	405.7	5.40	5.08	75.0	37.9	36.1	20.58
486.5	450.2	44.6	33.1	38.8	411.4	5.45	5.18	75.0	38.1	36.0	20.83

Table II

Performance of Couples Nos. 115B and 118 in Argon in Tester B under Comparable Conditions of Table I (germanium bismuth telluride P-Leg, lead telluride N-Leg, different back straps)

T_H T_c °C	Seebeck Micro. V / °C	Voltage Output Millivolts	Match Couple Amps	Res. Milliohms Total Couple	P Leg	N Leg	Correc'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm	Thermal * Watts / °C	Watts / °C cm.
				For Complete Couple No. 115B (plain stainless steel strap)								
417.6	360.2	150.6	0	-	-	-	14.39	0	-	-	0.0344	0.0172
408.7	-	75.3	18.11	4.16	1.517	2.615	17.35	1.363	7.85	2.072	-	-
414.3	-	75.3	18.36	4.11	1.475	2.588	17.35	1.382	7.96	2.048	-	-
				For P-Leg Alone (germanium bismuth telluride)								
414.2	150.1	62.1	0	-	-	-	7.58	0	-	-	0.0183	0.0184
405.4	-	34.6	18.11	-	1.517	-	8.78	0.626	7.14	1.512	-	-
411.1	-	35.0	18.36	-	1.475	-	8.89	0.642	7.23	1.471	-	-
				For N-Leg Alone (lead telluride)								
421.0	207.2	87.2	0	-	-	-	6.80	0	-	-	0.0162	0.0162
412.0	-	39.8	18.11	-	-	2.615	8.56	0.721	8.42	2.608	-	-
417.6	-	39.7	18.36	-	-	2.588	8.42	0.729	8.65	2.479	-	-

* Combined values for case of complete couple

Table II (continued)

T_H T_c °C	Seebeck Micro. V/°C	Voltage Output Millivolts	Match Couple Amps.	Res. Milliohms Total Couple	P leg	N leg	Corred'd Heat Watts	Elect'l Output Watts	Overall Eff. Percent	Resistiv'y* Milliohm cm	Thermal* Watts/°C	Watts/°C cm.
For Complete Couple No. 118 (recessed stainless steel strap)												
414.2	362.2	150.0	0	-	-	-	17.70	0	-	-	0.0427	0.0214
405.7	-	75.0	20.58	3.65	1.234	2.420	20.98	1.543	7.36	1.816	-	-
411.4	-	75.0	20.83	3.60	1.210	2.388	20.94	1.564	7.46	1.791	-	-
For P-Leg Alone (germanium bismuth telluride)												
409.0	154.8	63.3	0	-	-	-	9.29	0	-	-	0.0227	0.0229
400.0	-	37.9	20.58	-	1.234	-	10.99	0.779	7.09	1.230	-	-
405.7	-	38.1	20.83	-	1.210	-	10.88	0.793	7.29	1.206	-	-
For N-Leg Alone (lead telluride)												
419.5	204.5	85.8	0	-	-	-	8.40	0	-	-	0.0201	0.0201
411.4	-	36.1	20.58	-	-	2.420	9.98	0.756	7.58	2.410	-	-
417.1	-	36.0	20.83	-	-	2.388	10.06	0.750	7.46	2.380	-	-